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(54) Narrow MWD alpha-olefin copolymers.

(57) Novel copolymers of alpha-olefins have narrow MWD and comprise intramolecularly heterogeneous and intermolecularly homogeneous copolymer chains.

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NARROW MWD ALPHA-OLEFIN COPOLYMERS

Background of the Invention

The present invention relates to novel copolymers of alpha-olefins. More specifically, it relates to novel copolymers of ethylene with other alpha-olefins comprised of copolymer chains with compositions which are intramolecularly heterogeneous and intermolecularly homogeneous, as well as, to a process for making these copolymers and their use in lube oil and elastomer applications.

For convenience, certain terms that are repeated throughout the present specification are defined below:

a. Inter-CD defines the compositional variation, in terms of ethylene content, among polymer chains. It is expressed as the minimum deviation (analogous to a standard deviation) in terms of weight percent ethylene from the average ethylene composition for a given copolymer sample needed to include a given weight percent of the total copolymer sample which is obtained by excluding equal weight fractions from both ends of the distribution. The deviation need not be symmetrical. When expressed as a single number for example 15% Inter-CD, it shall mean the larger of the positive or negative deviations. For example, for a Gaussian compositional distribution, 95.5% of the polymer is within 20 wt.% ethylene of the mean if the standard deviation is 10%. The Inter-CD for 95.5 wt.% of the polymer is 20 wt.% ethylene for such a sample.

b. Intra-CD is the compositional variation, in terms of ethylene, within a copolymer chain. It is expressed as the minimum difference in weight (wt.) % ethylene that exists between two portions of a single copolymer chain, each portion comprising at least 5 weight % of the chain.

c. Molecular weight distribution (MWD) is a measure of the range of molecular weights within a given copolymer sample. It is characterized in terms of at least one of the ratios of weight average to number average molecular weight, \bar{M}_w/\bar{M}_n , and Z average to weight average molecular weight, \bar{M}_z/\bar{M}_w , where:

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

1
$$\bar{M}_n = \frac{\sum NiMi}{\sum Ni}, \text{ and}$$

2
$$\bar{M}_z = \frac{\sum NiMi^3}{\sum NiMi^2}, \text{ wherein}$$

3 Ni is the number of molecules of weight Mi .

4 d. Viscosity Index (V.I.) is the ability of a
5 lubricating oil to accommodate increases in temperature with
6 a minimum decrease in viscosity. The greater this ability,
7 the higher the V.I.

8 Ethylene-propylene copolymers, particularly elas-
9 tomers, are important commercial products. Two basic types
10 of ethylene-propylene copolymers are commercially available.
11 Ethylene-propylene copolymers (EPM) are saturated compounds
12 requiring vulcanization with free radical generators such as
13 organic peroxides. Ethylene-propylene terpolymers (EPDM)
14 contain a small amount of non-conjugated diolefin, such as
15 dicyclopentadiene; 1,4-hexadiene or ethylidene norbornene,
16 which provides sufficient unsaturation to permit vulcaniza-
17 tion with sulfur. Such polymers that include at least two
18 monomers, i.e., EPM and EPDM, will hereinafter be collec-
19 tively referred to as copolymers.

20 These copolymers have outstanding resistance to
21 weathering, good heat aging properties and the ability to be
22 compounded with large quantities of fillers and plasticizers
23 resulting in low cost compounds which are particularly useful
24 in automotive and industrial mechanical goods applications.
25 Typical automotive uses are tire sidewalls, inner tubes,
26 radiator and heater hose, vacuum tubing, weather stripping
27 and sponge doorseals and Viscosity Index (V.I.) improvers for
28 lubricating oil compositions. Typical mechanical goods uses
29 are for appliance, industrial and garden hoses, both molded
30 and extruded sponge parts, gaskets and seals and conveyor
31 belt covers. These copolymers also find use in adhesives,
32 appliance parts as in hoses and gaskets, wire and cable and
33 plastics blending.

1 As can be seen from the above, based on their
2 respective properties, EPM and EPDM find many, varied uses.
3 It is known that the properties of such copolymers which make
4 them useful in a particular application are, in turn,
5 determined by their composition and structure. For example,
6 the ultimate properties of an EPM or EPDM copolymer are
7 determined by such factors as composition, compositional
8 distribution, sequence distribution, molecular weight, and
9 molecular weight distribution (MWD).

10 The efficiency of peroxide curing depends on com-
11 position. As the ethylene level increases, it can be shown
12 that the "chemical" crosslinks per peroxide molecule in-
13 creases. Ethylene content also influences the rheological
14 and processing properties, because crystallinity, which acts
15 as physical crosslinks, can be introduced. The crystallinity
16 present at very high ethylene contents may hinder pro-
17 cessibility and may make the cured product too "hard" at
18 temperatures below the crystalline melting point to be useful
19 as a rubber..

20 Milling behavior of EPM or EPDM copolymers varies
21 radically with MWD. Narrow MWD copolymers crumble on a mill,
22 whereas broad MWD materials will band under conditions en-
23 countered in normal processing operations. At the shear
24 rates encountered in processing equipment, broader MWD co-
25 polymer has a substantially lower viscosity than narrower MWD
26 polymer of the same weight average molecular weight or low
27 strain rate viscosity.

28 Thus, there exists a continuing need for dis-
29 covering polymers with unique properties and compositions.
30 This is easily exemplified with reference to the area of V.I.
31 improvers for lubricating oils.

32 A motor oil should not be too viscous at low
33 temperatures so as to avoid serious frictional losses, faci-
34 litate cold starting and provide free oil circulation right
35 from engine startup. On the other hand, it should not be too
36 thin at working temperatures so as to avoid excessive engine
37 wear and excessive oil consumption. It is most desirable to

1 employ a lubricating oil which experiences the least vis-
2 cosity change with changes in temperature.

3 The ability of a lubricating oil to accommodate
4 increases in temperature with a minimum decrease in viscosity
5 is indicated by its Viscosity Index (V.I.). The greater this
6 ability, the higher the V.I.

7 Polymeric additives have been extensively used in
8 lubricating oil compositions to impart desirable viscosity-
9 temperature characteristics to the compositions. For exam-
10 ple, lubricating oil compositions which use EPM or EPDM
11 copolymers or, more generally, ethylene-(C₃-C₁₈) alpha-ole-
12 fin copolymers, as V.I. improvers are well known. These
13 additives are designed to modify the lubricating oil so that
14 changes in viscosity occurring with variations in tempera-
15 ture are kept as small as possible. Lubricating oils con-
16 taining such polymeric additives essentially maintain their
17 viscosity at higher temperatures while at the same time
18 maintaining desirable low viscosity fluidity at engine star-
19 ting temperatures.

20 Two important properties (although not the only
21 required properties as is known) of these additives relate to
22 low temperature performance and shear stability. Low tem-
23 perature performance relates to maintaining low viscosity at
24 very low temperatures, while shear stability relates to the
25 resistance of the polymeric additives to being broken down
26 into smaller chains.

27 The present invention is drawn to a novel copoly-
28 mer of ethylene and at least one other alpha-olefin monomer
29 which copolymer is intramolecularly heterogeneous and in-
30 termolecularly homogeneous. Furthermore, the MWD of the
31 copolymer is very narrow. It is well known that the breadth
32 of the MWD can be characterized by the ratios of various
33 molecular weight averages. For example, an indication of a
34 narrow MWD in accordance with the present invention is that
35 the ratio of weight to number average molecular weight
36 (\bar{M}_w/\bar{M}_n) is less than 2. Alternatively, a ratio of the Z-
37 average molecular weight to the weight average molecular

1 weight (\bar{M}_z/\bar{M}_w) of less than 1.8 typifies a narrow MWD in
2 accordance with the present invention. It is known that the
3 property advantages of copolymers in accordance with the
4 present invention are related to these ratios. Small weight
5 fractions of material can disproportionately influence these
6 ratios while not significantly altering the property advantages which depend on them. For instance, the presence of a
7 small weight fraction (e.g. 2%) of low molecular weight
8 copolymer can depress \bar{M}_n , and thereby raise \bar{M}_w/\bar{M}_n above 2
9 while maintaining \bar{M}_z/\bar{M}_w less than 1.8. Therefore, polymers,
10 in accordance with the present invention, are characterized
11 by having at least one of \bar{M}_w/\bar{M}_n less than 2 and \bar{M}_z/\bar{M}_w less than
12 1.8. The copolymer comprises chains within which the ratio
13 of the monomers varies along the chain length. To obtain the
14 intramolecular compositional heterogeneity and narrow MWD,
15 the copolymers in accordance with the present invention are
16 preferably made in a tubular reactor. It has been discovered
17 that to produce such copolymers requires the use of numerous
18 heretofore undisclosed method steps conducted within heretofore
19 undisclosed preferred ranges. Accordingly, the present
20 invention is also drawn to a method for making the novel
21 copolymers of the present invention.
22

23 Copolymers in accordance with the present invention
24 have been found to have improved properties in lubricating oil. Accordingly, the present invention is also drawn
25 to a novel oil additive composition which comprises basestock
26 mineral oil of lubricating viscosity containing an effective
27 amount of a viscosity index improver being copolymer in
28 accordance with the present invention.
29

1 Description of the Prior Art

2 Representative prior art dealing with tubular re-
3 actors to make copolymers are as follows:

4 In "Polymerization of ethylene and propylene to
5 amorphous copolymers with catalysts of vanadium oxychloride
6 and alkyl aluminum halides"; E. Junghanns, A. Gumboldt and G.
7 Bier; Makromol. Chem., v. 58 (12/12/62): 18-42, the use of a
8 tubular reactor to produce ethylene-propylene copolymer is
9 disclosed in which the composition varies along the chain
10 length. More specifically, this reference discloses the
11 production in a tubular reactor of amorphous ethylene-propy-
12 lene copolymers using Ziegler catalysts prepared from vana-
13 dium compound and aluminum alkyl. It is disclosed that at the
14 beginning of the tube ethylene is preferentially polymeriz-
15 ed, and if no additional make-up of the monomer mixture is
16 made during the polymerization the concentration of monomers
17 changes in favor of propylene along the tube. It is further
18 disclosed that since these changes in concentrations take
19 place during chain propagation, copolymer chains are pro-
20 duced which contain more ethylene on one end than at the ot-
21 her end. It is also disclosed that copolymers made in a tub-
22 chemically non-uniform, but fairly uniform as regards
23 ular weight distribution. Using the data reported
24 Figure 17 for copolymer prepared in the tube,
25 estimated that the \bar{M}_w/\bar{M}_n ratio for this copolyr
26 and from their Figure 18 that the intermolec
27 tional dispersity (Inter-CD, explained in d
28 this copolymer was greater than 15%.

29 "Laminar Flow Polymerization

30 J.F. Wehner; ACS Symposium Series 65
31 discloses the results of computer simu-
32 to determine the effect of tubular
33 merization with Ziegler catalysts
34 distribution of the polymer pro-
35 simulated was an elastomeric +
36 lene-1,4-hexadiene. On page
37 monomers have different re-

1 composition is obtained as the monomers are depleted. How-
2 ever, whether the composition varies inter-or intramolecu-
3 larly is not distinguished. In Table III on page 148, various
4 polymers having \bar{M}_w/\bar{M}_n of about 1.3 are predicted. In the
5 third paragraph on page 144, it is stated that as the tube
6 diameter increases, the polymer molecular weight is too low
7 to be of practical interest, and it is predicted that the
8 reactor will plug. It is implied in the first paragraph on
9 page 149 that the compositional dispersity produced in a tube
10 would be detrimental to product quality.

11 U.S. 3,681,306 to Wehner is drawn to a process for
12 producing ethylene/higher alpha-olefin copolymers having
13 good processability, by polymerization in at least two con-
14 secutive reactor stages. According to this reference, this
15 two-stage process provides a simple polymerization process
16 that permits tailor-making ethylene/alpha-olefin copolymers
17 having predetermined properties, particularly those con-
18 tributing to processability in commercial applications such
19 as cold-flow, high green strength and millability. According
20 to this reference, the inventive process is particularly
21 adapted for producing elastomeric copolymers, such as ethyl-
22 ene/propylene/5-ethylidene-2-norbornene, using any of the
23 coordination catalysts useful for making EPDM. The preferred
24 process uses one tubular reactor followed by one pot reactor.
25 However, it is also disclosed that one tubular reactor could
26 be used, but operated at different reaction conditions to
27 simulate two stages. As is seen from column 2, lines 14-20,
28 the inventive process makes polymers of broader MWD than
29 those made in a single stage reactor. Although intermediate
30 polymer from the first (pipeline) reactor is disclosed as
31 having a ratio of \bar{M}_w/\bar{M}_n of about 2, as disclosed in column 5,
32 lines 54-57, the final polymers produced by the inventive
33 process have an \bar{M}_w/\bar{M}_n of 2.4 to 5.

34 U.S. 3,625,658 to Closon discloses a closed circuit
35 tubular reactor apparatus with high recirculation rates of
36 the reactants which can be used to make elastomers of ethylene
37 and propylene. With particular reference to Fig.1, a hinged

1 support 10 for vertical leg 1 of the reactor allows for
2 horizontal expansion of the bottom leg thereof and prevents
3 harmful deformations due to thermal expansions, particularly
4 those experienced during reactor clean out.

5 U.S. 4,065,520 to Bailey et al discloses the use of
6 a batch reactor to make ethylene copolymers, including elas-
7 tomers, having broad compositional distributions. Several
8 feed tanks for the reactor are arranged in series, with the
9 feed to each being varied to make the polymer. The products
10 made have crystalline to semi-crystalline to amorphous re-
11 gions and gradient changes in between. The catalyst system
12 can use vanadium compounds alone or in combination with
13 titanium compound and is exemplified by vanadium oxy-tri-
14 chloride and diisobutyl aluminum chloride. In all examples
15 titanium compounds are used. In several examples hydrogen
16 and diethyl zinc, known transfer agents, are used. The
17 polymer chains produced have a compositionally disperse
18 first length and uniform second length. Subsequent lengths
19 have various other compositional distributions.

20 In "Estimation of Long-Chain Branching in Ethyl-
21 ene-Propylene Terpolymers from Infinite-Dilution Viscoelas-
22 tic Properties"; Y. Mitsuda, J. Schrag, and J. Ferry; J. Appl.
23 Pol. Sci., 18, 193 (1974) narrow MWD copolymers of ethylene-
24 propylene are disclosed. For example, in TABLE II on page
25 198, EPDM copolymers are disclosed which have \bar{M}_w/\bar{M}_n of from
26 1.19 to 1.32.

27 In "The Effect of Molecular Weight and Molecular
28 Weight Distribution on the Non-Newtonian Behavior of Ethyl-
29 ene-Propylene-Diene Polymers; Trans. Soc. Rheol., 14, 83
30 (1970); C.K. Shih, a whole series of compositionally homo-
31 geneous fractions were prepared and disclosed. For example,
32 the data in TABLE I discloses polymer Sample B having a high
33 degree of homogeneity. Also, based on the reported data, the
34 MWD of the sample is very narrow. However, the polymers are
35 not disclosed as having intramolecular dispersity.

36 Representative prior art dealing with ethylene-
37 alpha-olefin copolymers as lubricating oil additives are as

1 follows:

2 U.S. 3,697,429 to Engel et al discloses a blend of
3 ethylene-propylene copolymers having different ethylene con-
4 tents, i.e., a first copolymer of 40-83 wt.% ethylene and
5 \bar{M}_w/\bar{M}_n less than about 4.0 (preferably less than 2.6, e.g. 2.2)
6 and a second copolymer of 3-70 wt.% ethylene and \bar{M}_w/\bar{M}_n less
7 than 4.0, with the content of the first differing from the
8 second by at least 4 wt.% ethylene. These blends, when used
9 as V.I. improvers in lubricating oils, provide suitable low
10 temperature viscosity properties with minimal adverse inter-
11 action between the oil pour depressant and the ethylene-
12 propylene copolymer.

13 U.S. 3,522,180 discloses copolymers of ethylene
14 and propylene having a number average molecular weight of
15 10,000 to 40,000 and a propylene content of 20 to 70 mole
16 percent as V.I. improvers in lube oils. The preferred \bar{M}_w/\bar{M}_n
17 of these copolymers is less than about 4.0.

18 U.S. 3,691,078 to Johnston et al discloses the use
19 of ethylene-propylene copolymers containing 25-55 wt.% ethy-
20 lene which have a pendant index of 18-33 and an average
21 pendant size not exceeding 10 carbon atoms as lube oil
22 additives. The \bar{M}_w/\bar{M}_n is less than about 8. These additives
23 impart to the oil good low temperature properties with
24 respect to viscosity without adversely affecting pour point
25 depressants.

26 U.S. 3,551,336 to Jacobson et al discloses the use
27 of ethylene copolymers of 60-80 mole % ethylene, having no
28 more than 1.3 wt.% of a polymer fraction which is insoluble
29 in normal decane at 55°C as an oil additive. Minimization of
30 this decane-insoluble fraction in the polymer reduces the
31 tendency of the polymer to form haze in the oil, which haze
32 is evidence of low temperature instability probably caused by
33 adverse interaction with pour depressant additives. The
34 \bar{M}_w/\bar{M}_n of these copolymers is "surprisingly narrow" and is
35 less than about 4.0, preferably less than 2.6, e.g., 2.2.

1 Brief Description of the Drawings

2 The accompanying drawings depict, for illustration
3 purposes only, processes embodied by the present invention,
4 wherein:

5 Fig 1 is a schematic representation of a process
6 for producing polymer in accordance with the present inven-
7 tion,

8 Fig 2 schematically illustrates how the process
9 depicted in Fig 1 can be integrated into a lube oil additive
10 process,

11 Fig 3 is a graphical illustration of a technique
12 for determining Intra-CD of a copolymer,

13 Fig 4 graphically illustrates various copolymer
14 structures that can be attained using processes in accordance
15 with the present invention,

16 Fig 5 is a graphic representation of polymer con-
17 centration vs. residence time for consideration with Example
18 2 herein, and

19 Fig 6 is a graphic representation of intramolecular
20 compositional dispersity (Intra-CD) of copolymer chains made
21 with additional monomer feeds downstream of the reactor inlet
22 as in Example 3.

23

24 Detailed Description of the Invention

25 As already noted above, the present invention is
26 drawn to novel copolymer of ethylene and at least one other
27 alpha-olefin monomer which copolymer is intramolecularly
28 heterogeneous and intermolecularly homogeneous and has an
29 MWD characterized by at least one of \bar{M}_w/\bar{M}_n of less than 2 and
30 \bar{M}_z/\bar{M}_w of less than 1.8. More specifically, copolymer in
31 accordance with the present invention comprises intramole-
32 cularly heterogeneous chains wherein at least two portions of
33 an individual intramolecularly heterogeneous chain, each
34 portion comprising at least 5 weight percent of the chain,
35 differ in composition from one another by at least 5 weight
36 percent ethylene, wherein the intermolecular compositional
37 dispersity of the polymer is such that 95 wt.% of the polymer

1 chains have a composition 15% or less different in ethylene
 2 from the average weight percent ethylene composition, and
 3 wherein the copolymer is characterized by at least one of a
 4 ratio of \bar{M}_w/\bar{M}_n of less than 2 and a ratio of \bar{M}_z/\bar{M}_w of less than
 5 1.8.

6 Since the present invention is considered to be
 7 most preferred in the context of ethylene-propylene (EPM) or
 8 ethylene-propylene-diene (EPDM) copolymers, it will be des-
 9 cribed in detail in the context of EPM and/or EPDM.

10 Copolymer in accordance with the present invention
 11 is preferably made in a tubular reactor. When produced in a
 12 tubular reactor with monomer feed only at the tube inlet, it
 13 is known that at the beginning of the tubular reactor ethy-
 14 lene, due to its high reactivity, will be preferentially
 15 polymerized. However, the concentration of monomers changes
 16 along the tube in favor of propylene as the ethylene is
 17 depleted. The result is copolymer chains which are higher in
 18 ethylene concentration in the chain segments grown near the
 19 reactor inlet (as defined at the point at which the poly-
 20 merization reaction commences), and higher in propylene
 21 concentration in the chain segments formed near the reactor
 22 outlet. An illustrative copolymer chain of ethylene-propy-
 23 lene is schematically presented below with E representing
 24 ethylene constituents and P representing propylene con-
 25 stituents in the chain:

26 Segment: $\frac{1}{E-E-E-E-P} \frac{2}{E-E-E-P-P} \frac{3}{E-E-P-P-P} \frac{4}{E-P-P-P-P}$

28
 29 As can be seen from this illustrative schematic chain,
 30 the far left-hand segment (1) thereof represents that portion
 31 of the chain formed at the reactor inlet where the reaction
 32 mixture is proportionately richer in the more reactive con-
 33 stituent ethylene. This segment comprises four ethylene
 34 molecules and one propylene molecule. However, as subsequent
 35 segments are formed from left to right with the more reactive
 36 ethylene being depleted and the reaction mixture propor-
 37 tionately increasing in propylene concentration, the sub-

1 sequent chain segments become more concentrated in propy-
2 lene. The resulting chain is intramolecularly heterogen-
3 eous.

4 In the event that more than two monomers are used,
5 e.g., in the production of EPDM using a diene termonomer, for
6 purposes of describing the present invention all properties
7 related to homogeneity and heterogeneity will refer to the
8 relative ratio of ethylene to the other monomers in the chain.
9 The property, of the copolymer discussed herein, related to
10 intramolecular compositional dispersity (compositional var-
11 iation within a chain) shall be referred to as Intra-CD, and
12 that related to intermolecular compositional dispersity
13 (compositional variation between chains) shall be referred
14 to as Inter-CD.

15 For copolymers in accordance with the present in-
16 vention, composition can vary between chains as well as along
17 the length of the chain. An object of this invention is to
18 minimize the amount of interchain variation. The Inter-CD
19 can be characterized by the difference in composition between
20 some fraction of the copolymer and the average composition,
21 as well as by the total difference in composition between the
22 copolymer fractions containing the highest and lowest quan-
23 tity of ethylene. Techniques for measuring the breadth of the
24 Inter-CD are known as illustrated by Junghanns et al wherein
25 a p-xylene-dimethylformamide solvent/non-solvent was used to
26 fractionate copolymer into fractions of differing inter-
27 molecular composition. Other solvent/non-solvent systems
28 can be used such as hexane-2-propanol, as will be discussed
29 in more detail below.

30 The Inter-CD of copolymer in accordance with the
31 present invention is such that 95 wt.% of the copolymer chains
32 have an ethylene composition that differs from the average
33 weight percent ethylene composition by 15 wt.% or less. The
34 preferred Inter-CD is about 13% or less, with the most
35 preferred being about 10% or less. In comparison, Junghanns
36 et al found that their tubular reactor copolymer had an Inter-
37 CD of greater than 15 weight %.

1 Broadly, the Intra-CD of copolymer in accordance
 2 with the present invention is such that at least two portions
 3 of an individual intramolecularly heterogeneous chain, each
 4 portion comprising at least 5 weight percent of the chain,
 5 differ in composition from one another by at least 5 weight
 6 percent ethylene. Unless otherwise indicated, this property
 7 of Intra-CD as referred to herein is based upon at least two
 8 5 weight percent portions of copolymer chain. The Intra-CD
 9 of copolymer in accordance with the present invention can be
 10 such that at least two portions of copolymer chain differ by
 11 at least 10 weight percent ethylene. Differences of at least
 12 20 weight percent, as well as, of at least 40 weight percent
 13 ethylene are also considered to be in accordance with the
 14 present invention.

15 The experimental procedure for determining Intra-
 16 CD is as follows. First the Inter-CD is established as
 17 described below, then the polymer chain is broken into
 18 fragments along its contour and the Inter-CD of the fragments
 19 is determined. The difference in the two results is due to
 20 Intra-CD as can be seen in the illustrative example below.

21 Consider a heterogeneous sample polymer containing
 22 30 monomer units. It consists of 3 molecules designated A,
 23 B, C.

24 A EEEEEEEEEEEEEPPPEPPPEPPPEPPPPPP

25 B EEEEEEEEEEEEEPPPEPPPEPPPEPPPP

26 C EEPEEEEEEEEEPEEEPEEEPPPEPPPEPP

27 Molecule A is 36.8 wt. % ethylene, B is 46.6%, and
 28 C is 50% ethylene. The average ethylene content for the
 29 mixture is 44.3%. For this sample the Inter-CD is such that
 30 the highest ethylene polymer contains 5.7% more ethylene than
 31 the average while the lowest ethylene content polymer con-
 32 tains 7.5% less ethylene than the average. Or, in other
 33 words, 100 weight % of the polymer is within +5.7% and -7.5%
 34 ethylene about an average of 44.3%. Accordingly, the Inter-
 35 CD is 7.5% when the given weight % of the polymer is 100%. The
 36 distribution may be represented graphically as by curve 1 in
 37 Figure 3.

1 If the chains are broken into fragments, there will
2 be a new Inter-CD. For simplicity, consider first breaking
3 only molecule A into fragments shown by the slashes as
4 follows:

5 EEEEP/EEEEPE/EEPPE/EPPEP/PPEPP/PPPPP
6 Portions of 72.7%, 72.7%, 50%, 30.8%, 14.3% and 0% ethylene
7 are obtained. If molecules B and C are similarly broken and
8 the weight fractions of similar composition are grouped the
9 new Inter-CD shown by curve 2 in Figure 3 is obtained. The
10 difference between the two curves in the figure is due to
11 Intra-CD.

12 Consideration of such data, especially near the end
13 point ranges, demonstrates that for this sample at least 5%
14 of the chain contour represented by the cumulative weight %
15 range (a) differs in composition from another section by at
16 least 15% ethylene shown as (b), the difference between the
17 two curves. The difference in composition represented by (b)
18 cannot be intermolecular. If it were, the separation process
19 for the original polymer would have revealed the higher
20 ethylene contents seen only for the degraded chain.

21 The compositional differences shown by (b) and (d)
22 in the figure between original and fragmented chains give
23 minimum values for Intra-CD. The Intra-CD must be at least
24 that great, for chain sections have been isolated which are
25 the given difference in composition (b) or (d) from the
26 highest or lowest composition polymer isolated from the
27 original. We know in this example that the original polymer
28 represented at (b) had sections of 72.7% ethylene and 0%
29 ethylene in the same chain. It is highly likely that due to
30 the inefficiency of the fractionation process any real
31 polymer with Intra-CD examined will have sections of lower or
32 higher ethylene connected along its contour than that shown
33 by the end points of the fractionation of the original
34 polymer. Thus, this procedure determines a lower bound for
35 Intra-CD. To enhance the detection, the original whole
36 polymer can be fractionated (e.g., separate molecule A from
37 molecule B from molecule C in the hypothetical example) with

1 these fractions refractionated until they show no (or less)
2 Inter-CD. Subsequent fragmentation of this intermolecularly
3 homogeneous fraction now reveals the total Intra-CD. In
4 principle, for the example, if molecule A were isolated,
5 fragmented, fractionated and analyzed, the Intra-CD for the
6 chain sections would be $72.7-0\% = 72.7\%$ rather than $72.7-50\%$
7 $= 22.7\%$ seen by fractionating the whole mixture of molecules
8 A, B, and C.

9 In order to determine the fraction of a polymer
10 which is intramolecularly heterogeneous in a mixture of
11 polymers combined from several sources the mixture must be
12 separated into fractions which show no further heterogeneity
13 upon subsequent fractionation. These fractions are
14 subsequently fractured and fractionated to reveal which are
15 heterogeneous.

16 The fragments into which the original polymer is
17 broken should be large enough to avoid end effects and to give
18 a reasonable opportunity for the normal statistical distri-
19 bution of segments to form over a given monomer conversion
20 range in the polymerization. Intervals of ca 5 weight % of
21 the polymer are convenient. For example, at an average
22 polymer molecular weight of about 10^5 , fragments of ca 5000
23 molecular weight are appropriate. A detailed mathematical
24 analysis of plug flow or batch polymerization indicates that
25 the rate of change of composition along the polymer chain
26 contour will be most severe at high ethylene conversion near
27 the end of the polymerization. The shortest fragments are
28 needed here to show the low propylene content sections.

29 The best available technique for determination of
30 compositional dispersity for non-polar polymers is solvent/-
31 non-solvent fractionation which is based on the thermo-
32 dynamics of phase separation. This technique is described in
33 "Polymer Fractionation", M. Cantow editor, Academic 1967,
34 p.341 ff and in H. Inagaki, T. Tanaku, Developments in Polymer
35 Characterization, 3, 1 (1982). These are incorporated herein
36 by reference.

37 For non-crystalline copolymers of ethylene and
38 propylene, molecular weight governs insolubility more than

1 does composition in a solvent/non-solvent solution. High
2 molecular weight polymer is less soluble in a given solvent
3 mix. Also, there is a systematic correlation of molecular
4 weight with ethylene content for the polymers described
5 herein. Since ethylene polymerizes much more rapidly than
6 propylene, high ethylene polymer also tends to be high in
7 molecular weight. Additionally, chains rich in ethylene tend
8 to be less soluble in hydrocarbon/polar non-solvent mixtures
9 than propylene-rich chains. Thus the high molecular weight,
10 high ethylene chains are easily separated on the basis of
11 thermodynamics.

12 A fractionation procedure is as follows: Un-
13 fragmented polymer is dissolved in n-hexane at 23°C to form
14 ca a 1% solution (1 g polymer/100 cc hexane). Isopropyl
15 alcohol is titrated into the solution until turbidity appears
16 at which time the precipitate is allowed to settle. The
17 supernatant liquid is removed and the precipitate is dried by
18 pressing between Mylar® (polyethylene terephthalate) film at
19 150°C. Ethylene content is determined by ASTM method D-3900.
20 Titration is resumed and subsequent fractions are recovered
21 and analyzed until 100% of the polymer is collected. The
22 titrations are ideally controlled to produce fractions of 5-
23 10% by weight of the original polymer especially at the
24 extremes of composition.

25 To demonstrate the breadth of the distribution, the
26 data are plotted as % ethylene versus the cumulative weight
27 of polymer as defined by the sum of half the weight % of the
28 fraction of that composition plus the total weight % of the
29 previously collected fractions.

30 Another portion of the original polymer is broken
31 into fragments. A suitable method for doing this is by
32 thermal degradation according to the following procedure: In
33 a sealed container in a nitrogen-purged oven, a 2mm thick
34 layer of the polymer is heated for 60 minutes at 330°C. This
35 should be adequate to reduce a 10^5 molecular weight polymer
36 to fragments of ca 5000 molecular weight. Such degradation
37 does not change the average ethylene content of the polymer.

1 This polymer is fractionated by the same procedure as the high
2 molecular weight precursor. Ethylene content is measured, as
3 well as molecular weight on selected fractions.

4 Ethylene content is measured by ASTM-D3900 for
5 ethylene-propylene copolymers between 35 and 85 wt.% ethyl-
6 ene. Above 85% ASTM-D2238 can be used to obtain methyl group
7 concentrations which are related to percent ethylene in an
8 unambiguous manner for ethylene-propylene copolymers. When
9 comonomers other than propylene are employed no ASTM tests
10 covering a wide range of ethylene contents are available,
11 however, proton and carbon 13 nuclear magnetic resonance can
12 be employed to determine the composition of such polymers.
13 These are absolute techniques requiring no calibration when
14 operated such that all nuclei contribute equally to the
15 spectra. For ranges not covered by the ASTM tests for
16 ethylene-propylene copolymers, these nuclear magnetic reso-
17 nance methods can also be used.

18 Molecular weight and molecular weight distribution
19 are measured using a Waters 150 gel permeation chromatograph
20 equipped with a Chromatix KMX-6 on-line light scattering
21 photometer. The system is used at 135°C with 1,2,4 tri-
22 chlorobenzene as mobile phase. Showdex (Showa-Denko Amer-
23 ica, Inc.) polystyrene gel columns 802, 803, 804 and 805 are
24 used. This technique is discussed in "Liquid Chromatography
25 of Polymers and Related Materials III", J. Cazes editor.
26 Marcel Dekker, 1981, p. 207 (incorporated herein by refer-
27 ence). No corrections for column spreading are employed;
28 however, data on generally accepted standards, e.g., Nation-
29 al Bureau of Standards Polyethene 1484 and anionically pro-
30 duced hydrogenated polyisoprenes (an alternating ethylene-
31 propylene copolymer) demonstrate that such corrections on
32 \bar{M}_w/\bar{M}_n or \bar{M}_z/\bar{M}_w are less than .05 unit. \bar{M}_w/\bar{M}_n is calculated
33 from an elution time-molecular weight relationship whereas
34 \bar{M}_z/\bar{M}_w is evaluated using the light scattering photometer.
35 The numerical analyses can be performed using the commer-
36 cially available computer software GPC2, MOLWT2 available
37 from LDC/Milton Roy-Riviera Beach, Florida.

1 As already noted, copolymers in accordance with the
2 present invention are comprised of ethylene and at least one
3 other alpha-olefin. It is believed that such alpha-olefins
4 could include those containing 3 to 18 carbon atoms, e.g.,
5 propylene, butene-1, pentene-1, etc. Alpha-olefins of 3 to
6 6 carbons are preferred due to economic considerations. The
7 most preferred copolymers in accordance with the present
8 invention are those comprised of ethylene and propylene or
9 ethylene, propylene and diene.

10 As is well known to those skilled in the art,
11 copolymers of ethylene and higher alpha-olefins such as
12 propylene often include other polymerizable monomers. Typi-
13 cal of these other monomers may be non-conjugated dienes such
14 as the following non-limiting examples:

- 15 a. straight chain acyclic dienes such as: 1,4-
16 hexadiene; 1,6-octadiene; &
- 17 b. branched chain acyclic dienes such as: 5-
18 methyl-1,4-hexadiene; 3,7-dimethyl-1,6-octa-
19 diene; 3,7-dimethyl-1,7-octadiene and the mixed
20 isomers of dihydro-myrcene and dihydroocinene;
- 21 c. single ring alicyclic dienes such as: 1,4-
22 cyclohexadiene; 1,5-cyclooctadiene; and 1,5-
23 cyclododecadiene;
- 24 d. multi-ring alicyclic fused and bridged ring
25 dienes such as: tetrahydroindene; methyltetrahy-
26 droindene; dicyclopentadiene; bicyclo-(2,2,1) -
27 hepta-2,5-diene; alkenyl, alkylidene, cycloalkenyl
28 and cycloalkylidene norbornenes such as 5-methy-
29 lene-2-norbornene (MNB), 5-ethylidene-2-nor-
30 bornene (ENB), 5-propyl-2-norbornene, 5-isopropyl-
31 idene-2-norbornene, 5-(4-cyclopentenyl) -2-
32 norbornene; 5-cyclohexylidene-2-norbornene.

33 Of the non-conjugated dienes typically used to
34 prepare these copolymers, dienes containing at least one of
35 the double bonds in a strained ring are preferred. The most
36 preferred diene is 5-ethylidene-2-norbornene (ENB). The
37 amount of diene (wt. basis) in the copolymer could be from

1 about 0% to 20% with 0% to 15% being preferred. The most
2 preferred range is 0% to 10%.

3 As already noted, the most preferred copolymer in
4 accordance with the present invention is ethylene-propylene
5 or ethylene-propylene-diene. In either event, the average
6 ethylene content of the copolymer could be as low as about 10%
7 on a weight basis. The preferred minimum is about 25%. A more
8 preferred minimum is about 30%. The maximum ethylene content
9 could be about 90% on a weight basis. The preferred maximum
10 is about 85%, with the most preferred being about 80%.

11 The molecular weight of copolymer made in accor-
12 dance with the present invention can vary over a wide range.
13 It is believed that the weight average molecular weight could
14 be as low as about 2,000. The preferred minimum is about
15 10,000. The most preferred minimum is about 20,000. It is
16 believed that the maximum weight average molecular weight
17 could be as high as about 12,000,000. The preferred maximum
18 is about 1,000,000. The most preferred maximum is about
19 750,000.

20 Another feature of copolymer made in accordance
21 with the present invention is that the molecular weight
22 distribution (MWD) is very narrow, as characterized by at
23 least one of a ratio of \bar{M}_w/\bar{M}_n of less than 2 and a ratio of
24 \bar{M}_z/\bar{M}_w of less than 1.8. As relates to EPM and EPDM, some
25 typical advantages of such copolymers having narrow MWD are
26 greater resistance to shear degradation, and when compounded
27 and vulcanized, faster cure and better physical properties
28 than broader MWD materials. Particularly for oil additive
29 applications, the preferred copolymers have \bar{M}_w/\bar{M}_n less than
30 about 1.6, with less than about 1.4 being most preferred. The
31 preferred \bar{M}_z/\bar{M}_w is less than about 1.5, with less than about
32 1.3 being most preferred.

33 Processes in accordance with the present invention
34 produce copolymer by polymerization of a reaction mixture
35 comprised of catalyst, ethylene and at least one additional
36 alpha-olefin monomer. Solution polymerizations are pre-
37 ferred.

1 Any known solvent for the reaction mixture that is
2 effective for the purpose can be used in conducting soluti n
3 polymerizations in accordance with the present invention.
4 For example, suitable solvents would be hydrocarbon solvents
5 such as aliphatic, cycloaliphatic and aromatic hydrocarbon
6 solvents, or halogenated versions of such solvents. The
7 preferred solvents are C₁₂ or lower, straight chain or
8 branched chain, saturated hydrocarbons, C₅ to C₉ saturated
9 alicyclic or aromatic hydrocarbons or C₂ to C₆ halogenated
10 hydrocarbons. Most preferred are C₁₂ or lower, straight
11 chain or branched chain hydrocarbons, particularly hexane.
12 Nonlimiting illustrative examples of solvents are butane,
13 pentane, hexane, heptane, cyclopentane, cyclohexane, cyclo-
14 heptane, methyl cyclopentane, methyl cyclohexane, isooctane,
15 benzene, toluene, xylene, chloroform, chlorobenzenes, tet-
16 rachloroethylene, dichloroethane and trichloroethane.

17 These processes are carried out in a mix-free
18 reactor system, which is one in which substantially no mixing
19 occurs between portions of the reaction mixture that contain
20 polymer chains initiated at different times. Suitable re-
21 actors are a continuous flow tubular or a stirred batch
22 reactor. A tubular reactor is well known and is designed to
23 minimize mixing of the reactants in the direction of flow. As
24 a result, reactant concentration will vary along the reactor
25 length. In contrast, the reaction mixture in a continuous
26 flow stirred tank reactor (CFSTR) is blended with the incom-
27 ing feed to produce a solution of essentially uniform com-
28 position everywhere in the reactor. Consequently, the grow-
29 ing chains in a portion of the reaction mixture will have a
30 variety of ages and thus a single CFSTR is not suitable for
31 the process of this invention. However, it is well known that
32 3 or more stirred tanks in series with all of the catalyst fed
33 to the first reactor can approximate the performance of a
34 tubular reactor. Accordingly, such tanks in series are
35 considered to be in accordance with the present invention.

36 A batch reactor is a suitable vessel, preferably
37 equipped with adequate agitation, to which the catalyst,

1 solvent, and monomer are added at the start of the poly-
2 merization. The charge of reactants is then left to poly-
3 merize for a time long enough to produce the desired product.
4 For economic reasons, a tubular reactor is preferred to a
5 batch reactor for carrying out the processes of this inven-
6 tion.

7 In addition to the importance of the reactor sys-
8 tem to make copolymers in accordance with the present in-
9 vention, the polymerization should be conducted such that:

- 10 a. the catalyst system produces essentially one
- 11 active catalyst species,
- 12 b. the reaction mixture is essentially free of
- 13 chain transfer agents, and
- 14 c. the polymer chains are essentially all ini-
- 15 tiated simultaneously, which is at the same time
- 16 for a batch reactor or at the same point along the
- 17 length of the tube for a tubular reactor.

18 The desired polymer can be obtained if additional
19 solvent and reactants (e.g., at least one of the ethylene,
20 alpha-olefin and diene) are added either along the length of
21 a tubular reactor or during the course of polymerization in
22 a batch reactor. Operating in this fashion may be desirable
23 in certain circumstances to control the polymerization rate
24 or polymer composition. However, it is necessary to add
25 essentially all of the catalyst at the inlet of the tube or
26 at the onset of batch reactor operation to meet the re-
27 quirement that essentially all polymer chains are initiated
28 simultaneously.

29 Accordingly, processes in accordance with the pre-
30 sent invention are carried out:

- 31 (a) in at least one mix-free reactor,
- 32 (b) using a catalyst system that produces essen-
- 33 tially one active catalyst species,
- 34 (c) using at least one reaction mixture which is
- 35 essentially transfer agent-free, and
- 36 (d) in such a manner and under conditions suffi-
- 37 cient to initiate propagation of essentially all polymer

1 chains simultaneously.

2 Since the tubular reactor is the preferred reactor
3 system for carrying out processes in accordance with the
4 present invention, the following illustrative descriptions
5 and examples are drawn to that system, but will apply to other
6 reactor systems as will readily occur to the artisan having
7 the benefit of the present disclosure.

8 In practicing processes in accordance with the
9 present invention, use is preferably made of at least one
10 tubular reactor. Thus, in its simplest form, such a process
11 would make use of but a single reactor. However, as would
12 readily occur to the artisan having the benefit of the present
13 disclosure, more than one reactor could be used, either in
14 parallel for economic reasons, or in series with multiple
15 monomer feed to vary intramolecular composition.

16 For example, various structures can be prepared by
17 adding additional monomer(s) during the course of the poly-
18 merization, as shown in Fig. 4, wherein composition is plotted
19 versus position along the contour length of the chain. The
20 Intra-CD of curve 1 is obtained by feeding all of the monomers
21 at the tubular reactor inlet or at the start of a batch
22 reaction. In comparison, the Intra-CD of curve 2 can be made
23 by adding additional ethylene at a point along the tube or,
24 in a batch reactor, where the chains have reached about half
25 their length. The Intra-CD's of Curve 3 requires multiple
26 feed additions. The Intra-CD of curve 4 can be formed if
27 additional comonomer rather than ethylene is added. This
28 structure permits a whole ethylene composition range to be
29 omitted from the chain. In each case, a third or more
30 comonomers may be added.

31 The composition of the catalyst used to produce
32 alpha-olefin copolymers has a profound effect on copolymer
33 product properties such as compositional dispersity and MWD.
34 The catalyst utilized in practicing processes in accordance
35 with the present invention should be such as to yield
36 essentially one active catalyst species in the reaction
37 mixture. More specifically, it should yield one primary

1 active catalyst species which provides for substantially all
2 of the polymerization reaction. Additional active catalyst
3 species could be present, provided the copolymer product is
4 in accordance with the present invention, e.g., narrow MWD
5 and Inter-CD. It is believed that such additional active
6 catalyst species could provide as much as 35% (weight) of the
7 total copolymer. Preferably, they should account for about
8 10% or less of the copolymer. Thus, the essentially one
9 active species should provide for at least 65% of the total
10 copolymer produced, preferably for at least 90% thereof. The
11 extent to which a catalyst species contributes to the
12 polymerization can be readily determined using the below-
13 described techniques for characterizing catalyst according
14 to the number of active catalyst species.

15 Techniques for characterizing catalyst according
16 to the number of active catalyst species are within the skill
17 of the art, as evidenced by an article entitled "Ethylene-
18 Propylene Copolymers. Reactivity Ratios, Evaluation and
19 Significance", C. Cozewith and G. Ver Strate, Macromole-
20 cules, 4, 482 (1971), which is incorporated herein by ref-
21 erence.

22 It is disclosed by the authors that copolymers made
23 in a continuous flow stirred reactor should have an MWD
24 characterized by $\bar{M}_w/\bar{M}_n=2$ and a narrow Inter-CD when one
25 active catalyst species is present. By a combination of
26 fractionation and gel permeation chromatography (GPC) it is
27 shown that for single active species catalysts the composi-
28 tions of the fractions vary no more than $\pm 3\%$ about the average
29 and the MWD (weight to number average ratio) for these samples
30 approaches two (2). It is this latter characteristic (\bar{M}_w/\bar{M}_n
31 of about 2) that is deemed the more important in identifying
32 a single active catalyst species. On the other hand, other
33 catalysts gave copolymer with an Inter-CD greater than $\pm 10\%$
34 about the average and multi-modal MWD often with \bar{M}_w/\bar{M}_n
35 greater than 10. These other catalysts are deemed to have
36 more than one active species.

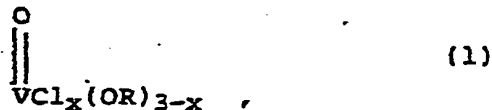
37 Catalyst systems to be used in carrying out pro-

cesses in accordance with the present invention may be Ziegler catalysts, which may typically include:

(a) a compound of a transition metal, i.e., a metal of Groups I-B, III-B, IVB, VB, VIB, VIIB and VIII of the Periodic Table, and (b) an organometal compound of a metal of Groups I-A, II-A, II-B and III-A of the Periodic Table.

The preferred catalyst system in practicing processes in accordance with the present invention comprises hydrocarbon-soluble vanadium compound in which the vanadium valence is 3 to 5 and organo-aluminum compound, with the proviso that the catalyst system yields essentially one active catalyst species as described above. At least one of the vanadium compound/organo-aluminum pair selected must also contain a valence-bonded halogen.

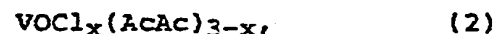
In terms of formulas, vanadium compounds useful in practicing processes in accordance with the present invention could be:



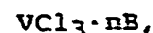
where $x = 0-3$ and $R =$ a hydrocarbon radical;



where $\text{AcAc} =$ acetyl acetate;



where $x = 1$ or 2 ; and



where $n = 2-3$ and $\text{B} =$ Lewis base capable of making hydrocarbon-soluble complexes with VCl_3 , such as tetrahydrofuran, 2-methyl-tetrahydrofuran and dimethyl pyridine.

1 In formula 1 above, R preferably represents a C₁ to
 2 C₁₀ aliphatic, alicyclic or aromatic hydrocarbon radical
 3 such as ethyl (Et), phenyl, isopropyl, butyl, propyl, n-
 4 butyl, i-butyl, t-butyl, hexyl, cyclohexyl, octyl, naphthyl,
 5 etc. Non-limiting, illustrative examples of formula (1) and
 6 (2) compounds are vanadyl trihalides, alkoxy halides and
 7 alkoxides such as VOCl₃, VOCl₂(OBu) where Bu = butyl, and
 8 VO(OC₂H₅)₃. The most preferred vanadium compounds are VCl₄,
 9 VOCl₃, and VOCl₂(OR).

10 As already noted, the co-catalyst is preferably
 11 organo-aluminum compound. In terms of chemical formulas,
 12 these compounds could be as follows:

13 AlR₃, Al(OR')R₂
 14 Al R₂Cl, R₂Al-O-AlR₂
 15 AlR'RCl AlR₂I
 16 Al₂R₃Cl₃, and
 17 AlRCl₂,

18 where R and R' represent hydrocarbon radicals, the
 19 same or different, as described above with respect to the
 20 vanadium compound formula. The most preferred organo-
 21 aluminum compound is an aluminum alkyl sesquichloride such as
 22 Al₂Et₃Cl₃ or Al₂(iBu)₃Cl₃.

23 In terms of performance, a catalyst system com-
 24 prised of VCl₄ and Al₂R₃Cl₃, preferably where R is ethyl, has
 25 been shown to be particularly effective. For best catalyst
 26 performance, the molar amounts of catalyst components added
 27 to the reaction mixture should provide a molar ratio of
 28 aluminum/vanadium (Al/V) of at least about 2. The preferred
 29 minimum Al/V is about 4. The maximum Al/V is based primarily
 30 on the considerations of catalyst expense and the desire to
 31 minimize the amount of chain transfer that may be caused by
 32 the organo-aluminum compound (as explained in detail below).
 33 Since, as is known certain organo-aluminum compounds act as
 34 chain transfer agents, if too much is present in the reaction
 35 mixture the \bar{M}_w/\bar{M}_n of the copolymer may rise above 2. Based
 36 on these considerations, the maximum Al/V could be about 25,
 37 however, a maximum of about 17 is more preferred. The most

1 preferred maximum is about 15.

2 Chain transfer agents for the Ziegler-catalyzed
3 polymerization of alpha-olefins are well known and are il-
4 lustrated, by way of example, by hydrogen or diethyl zinc for
5 the production of EPM and EPDM. Such agents are very commonly
6 used to control the molecular weight of EPM and EPDM produced
7 in continuous flow stirred reactors. For the essentially
8 single active species Ziegler catalyst systems used in ac-
9 cordance with the present invention, addition of chain
10 transfer agents to a CFSTR reduces the polymer molecular
11 weight but does not affect the molecular weight distribution.
12 On the other hand, chain transfer reactions during tubular
13 reactor polymerization in accordance with the present
14 invention broaden polymer molecular weight distribution and
15 Inter-CD. Thus the presence of chain transfer agents in the
16 reaction mixture should be minimized or omitted altogether.
17 Although difficult to generalize for all possible reactions,
18 the amount of chain transfer agent used should be limited to
19 those amounts that provide copolymer product in accordance
20 with the desired limits as regards MWD and compositional
21 dispersity. It is believed that the maximum amount of chain
22 transfer agent present in the reaction mixture could be as
23 high as about 0.2 mol/mol of transition metal, e.g.,
24 vanadium, again provided that the resulting copolymer pro-
25 duct is in accordance with the desired limits as regards MWD
26 and compositional dispersity. Even in the absence of added
27 chain transfer agent, chain transfer reactions can occur
28 because propylene and the organo-aluminum cocatalyst can
29 also act as chain transfer agents. In general, among the
30 organo-aluminum compounds that in combination with the vana-
31 dium compound yield just one active species, the organo-
32 aluminum compound that gives the highest copolymer molecular
33 weight at acceptable catalyst activity should be chosen.
34 Furthermore, if the Al/V ratio has an effect on the molecular
35 weight of copolymer product, that Al/V should be used which
36 gives the highest molecular weight also at acceptable cata-
37 lyst activity. Chain transfer with propylene can best be

1 limited by avoiding excessive temperature during the poly-
2 merization as described below.

3 Molecular weight distribution and Inter-CD are
4 narrowest when no catalyst deactivation occurs during the course of
5 the polymerization which leads to termination of growing
6 chains. Presently it is known that the vanadium-based catalyst
7 catalysts used in accordance with the present invention are
8 subject to such deactivation reactions which depend to an
9 extent upon the composition of the catalyst. Although the
10 relationship between active catalyst lifetime and catalyst
11 system composition is not known at present, for any given
12 catalyst, deactivation can be reduced by using the shortest
13 residence time and lowest temperature in the reactor that
14 will produce the desired monomer conversions.

15 Polymerizations in accordance with the present
16 invention should be conducted in such a manner and under
17 conditions sufficient to initiate propagation of essentially
18 all copolymer chains simultaneously. This can be accom-
19 plished by utilizing the process steps and conditions des-
20 cribed below.

21 The catalyst components are preferably premixed,
22 that is, reacted to form active catalyst outside of the
23 reactor, to ensure rapid chain initiation. Aging of the
24 premixed catalyst system, that is, the time spent by the
25 catalyst components (e.g., vanadium compound and organo-
26 aluminum) in each other's presence outside of the reactor,
27 should preferably be kept within limits. If not aged for a
28 sufficient period of time, the components will not have
29 reacted with each other sufficiently to yield an adequate
30 quantity of active catalyst species, with the result of non-
31 simultaneous chain initiation. Also, it is known that the
32 activity of the catalyst species will decrease with time so
33 that the aging must be kept below a maximum limit. It is
34 believed that the minimum aging period, depending on such
35 factors as concentration of catalyst components, temperature
36 and mixing equipment, could be as low as about .1 second. The
37 preferred minimum aging period is about .5 second, while the

1 most preferred minimum aging period is about 1 second. While
2 the maximum aging period could be higher, for the preferred
3 vanadium/organo-aluminum catalyst system the preferred
4 maximum is about 200 seconds. A more preferred maximum is
5 about 100 seconds. The most preferred maximum aging period
6 is about 50 seconds. The premixing could be performed at low
7 temperature such as 40°C or below. It is preferred that the
8 premixing be performed at 25°C or below, with 15°C or below
9 being most preferred.

10 The temperature of the reaction mixture should also
11 be kept within certain limits. The temperature at the reactor
12 inlet should be high enough to provide complete, rapid chain
13 initiation at the start of the polymerization reaction. The
14 length of time the reaction mixture spends at high tempera-
15 ture must be short enough to minimize the amount of un-
16 desirable chain transfer and catalyst deactivation reac-
17 tions.

18 Temperature control of the reaction mixture is
19 complicated somewhat by the fact that the polymerization
20 reaction generates large quantities of heat. This problem
21 is, preferably, taken care of by using prechilled feed to the
22 reactor to absorb the heat of polymerization. With this
23 technique, the reactor is operated adiabatically and the
24 temperature is allowed to increase during the course of
25 polymerization. As an alternative to feed prechill, heat can
26 be removed from the reaction mixture, for example, by a heat
27 exchanger surrounding at least a portion of the reactor or by
28 well-known autorefrigeration techniques in the case of batch
29 reactors or multiple stirred reactors in series.

30 If adiabatic reactor operation is used, the inlet
31 temperature of the reactor feed could be about from -50°C to
32 500°C. It is believed that the outlet temperature of the
33 reaction mixture could be as high as about 200°C. The
34 preferred maximum outlet temperature is about 70°C. The most
35 preferred maximum is about 50°C. In the absence of reactor
36 cooling, such as by a cooling jacket, to remove the heat of
37 polymerization, it has been determined that the temperature

1 of the reaction mixture will increase from reactor inlet to
2 outlet by about 13°C per weight percent of copolymer in the
3 reaction mixture (weight of copolymer per weight of solvent).

4 Having the benefit of the above disclosure, it
5 would be well within the skill of the art to determine the
6 operating temperature conditions for making copolymer in ac-
7 cordance with the present invention. For example, assume an
8 adiabatic reactor and an outlet temperature of 35°C are
9 desired for a reaction mixture containing 5% copolymer. The
10 reaction mixture will increase in temperature by about 13°C
11 for each weight percent copolymer or 5 weight percent x
12 13°C/wt.% = 65°C. To maintain an outlet temperature of 35°C,
13 it will thus require a feed that has been prechilled to 35°C -
14 65°C = -30°C. In the instance that external cooling is used
15 to absorb the heat of polymerization, the feed inlet tempera-
16 ture could be higher with the other temperature constraints
17 described above otherwise being applicable.

18 Because of heat removal and reactor temperature
19 limitations, the preferred maximum copolymer concentration
20 at the reactor outlet is 25 wt./100 wt. diluent. The most
21 preferred maximum concentration is 15 wt./100 wt. There is no
22 lower limit to concentration due to reactor operability, but
23 for economic reasons it is preferred to have a copolymer
24 concentration of at least 2 wt./100 wt. Most preferred is a
25 concentration of at least 3 wt./100 wt.

26 The rate of flow of the reaction mixture through
27 the reactor should be high enough to provide good mixing of
28 the reactants in the radial direction and minimize mixing in
29 the axial direction. Good radial mixing is beneficial not
30 only to both the Intra- and Inter-CD of the copolymer chains
31 but also to minimize radial temperature gradients due to the
32 heat generated by the polymerization reaction. Radial tem-
33 perature gradients will tend to broaden the molecular weight
34 distribution of the copolymer since the polymerization rate
35 is faster in the high temperature regions resulting from poor
36 heat dissipation. The artisan will recognize that achieve-
37 ment of these objectives is difficult in the case of highly

1 viscous solutions. This problem can be overcome to some
2 extent through the use of radial mixing devices such as static
3 mixers (e.g., those produced by the Kenics Corporation).

4 It is believed that residence time of the reaction
5 mixture in the mix-free reactor can vary over a wide range.
6 It is believed that the minimum could be as low as about 1
7 second. A preferred minimum is about 10 seconds. The most
8 preferred minimum is about 15 seconds. It is believed that
9 the maximum could be as high as about 3600 seconds. A
10 preferred maximum is about 1800 seconds. The most preferred
11 maximum is about 900 seconds.

12 With reference to the accompanying drawings, par-
13 ticularly Fig 1, reference numeral 1 generally refers to a
14 premixing device for premixing the catalyst components. For
15 purposes of illustration, it is assumed that a copolymer of
16 ethylene and propylene (EPM) is to be produced using as
17 catalyst components vanadium tetrachloride and ethyl alu-
18 minum sesqui chloride. The polymerization is an adiabatic,
19 solution polymerization process using hexane solvent for
20 both the catalyst system and the reaction mixture.

21 The premixing device 1 comprises a temperature
22 control bath 2, a fluid flow conduit 3 and mixing device 4
23 (e.g., a mixing tee). To mixing device 4 are fed hexane
24 solvent, vanadium tetrachloride and ethyl aluminum sesqui-
25 chloride through feed conduits 5, 6 and 7, respectively. Upon
26 being mixed in mixing device 4, the resulting catalyst
27 mixture is caused to flow within conduit 3, optionally in the
28 form of a coiled tube, for a time long enough to produce the
29 active catalyst species at the temperature set by the tem-
30 perature bath. The temperature of the bath is set to give the
31 desired catalyst solution temperature in conduit 3 at the
32 outlet of the bath.

33 Upon leaving the premixing device, the catalyst
34 solution flows through conduit 8 into mixing zone 9 to provide
35 an intimate mixing with hexane solvent and reactants (ethy-
36 lene and propylene) which are fed through conduit 10. Any
37 suitable mixing device can be used, such as a mechanical

1 mixer, orifice mixer or mixing tee. For economic reasons, the
2 mixing tee is preferred. The residence time of the reaction
3 mixture in mixing zone 9 is kept short enough to prevent
4 significant polymer formation therein before being fed
5 through conduit 11 to tubular reactor 12. Alternatively,
6 streams 8 and 10 can be fed directly to the inlet of reactor
7 12 if the flow rates are high enough to accomplish the desired
8 level of intimate mixing. The hexane with dissolved monomers
9 may be cooled upstream of mixing zone 9 to provide the desired
10 feed temperature at the reactor inlet.

11 Tubular reactor 12 is shown with optional, inter-
12 mediate feed points 13-15 where additional monomers (e.g.,
13 ethylene as shown) and/or hexane can be fed to the reactor.
14 The optional feeds would be used in the instance where it
15 would be desirable to control the Intra-CD. While the reactor
16 can be operated adiabatically, if desired or necessary to
17 maintain reaction mixture temperature within desired limits,
18 external cooling means such as a cooling jacket surrounding
19 at least a portion of the reactor system 12 can be provided.

20 The copolymer chains formed in accordance with
21 the present invention are dispersed within the reaction
22 mixture.

23 With reference to Fig 2 which schematically illus-
24 trates a process for mixing copolymer with lube oil, copoly-
25 mer product from reactor 12 is fed through conduit 16 to
26 deashing section 17 wherein catalyst residues are removed
27 from the reaction mixture in a known manner (known as de-
28 ashing). The vanadium and aluminum compound residues are
29 removed by reacting them with water to form hydrocarbon-
30 insoluble hydroxides and then extracting the hydroxides into
31 dilute acid.

32 After separating the aqueous and hydrocarbon phas-
33 es, for instance in a gravity settler, the polymer solution,
34 which primarily contains solvent, unreacted monomers and
35 copolymer product (EPM) is fed through conduit 18 to lube oil
36 mixing tank 19. Of course, tank 19 could be a staged series
37 of tanks. Hot lube oil is fed through conduit 20 to mixing

1 tank 19, wherein the remaining reaction mixture is heated up
2 such that the remaining hexane and unreacted monomers are
3 vaporized and removed through recycle conduit 21 through
4 which they flow back for reuse in premixing device 1 following
5 suitable purification to remove any catalyst poisons. The
6 copolymer product, being hydrocarbon-soluble, is now present
7 in the lube oil and is removed from tank 19 as a copolymer-
8 in-oil solution.

9 Alternatively, the copolymer solution from the
10 gravity settler can be steam distilled with subsequent
11 extrusion drying of the polymer and then mixed with a
12 hydrocarbon mineral oil diluent to produce an oil additive
13 concentrate or lube oil additive.

14 Having thus described the above illustrative re-
15 actor system, it will readily occur to the artisan that many
16 variations can be made within the scope of the present
17 invention. For example, the placement and number of multiple
18 feed sites, the choice of temperature profile during poly-
19 merization and the concentrations of reactants can be varied
20 to suit the end-use application.

21 By practicing processes in accordance with the
22 present invention, alpha-olefin copolymers having very nar-
23 row MWD can be made by direct polymerization. Although narrow
24 MWD copolymers can be made using other known techniques, such
25 as by fractionation or mechanical degradation, these techni-
26 ques are considered to be impractical to the extent of being
27 unsuitable for commercial-scale operation. As regards EPDM
28 made in accordance with the present invention, the products
29 have enhanced cure properties at a given Mooney Viscosity. As
30 regards EPM, the products have good shear stability and
31 excellent low temperature properties which make them es-
32 pecially suitable for lube oil applications. For lube oil
33 applications, the narrower the MWD of the polymer, the better
34 the copolymer is considered to be.

35 A lubricating oil composition in accordance with
36 the present invention comprises a major amount of basestock
37 lubricating oil (lube oil) of lubricating viscosity which

1 contains an effective amount of viscosity index improver
2 being a copolymer of ethylene and at least one other alpha-
3 olefin as described in detail above. More specifically, the
4 copolymer should have a MWD characterized by at least one of
5 a ratio of \bar{M}_w/\bar{M}_n of less than 2 and a ratio of \bar{M}_z/\bar{M}_w of less
6 than 1.8. The preferred ratio of \bar{M}_w/\bar{M}_n is less than about
7 1.6, with less than about 1.4 being preferred. The preferred
8 \bar{M}_z/\bar{M}_w is less than about 1.5, with less than about 1.3 being
9 most preferred.

10 It is preferred that the Intra-CD of the copolymer
11 is such that at least two portions of an individual intra-
12 molecularly heterogeneous chain, each portion comprising at
13 least 5 weight percent of said chain, differ in composition
14 from one another by at least 5 weight percent ethylene. The
15 Intra-CD can be such that at least two portions of copolymer
16 chain differ by at least 10 weight percent ethylene. Dif-
17 ferences of at least 20 weight percent, as well as, 40 weight
18 percent ethylene are also considered to be in accordance with
19 the present invention.

20 It is also preferred that the Inter-CD of the
21 copolymer is such that 95 wt.% of the copolymer chains have
22 an ethylene composition that differs from the copolymer
23 average weight percent ethylene composition by 15 wt.% or
24 less. The preferred Inter-CD is about 13% or less, with the
25 most preferred being about 10% or less.

26 In a most preferred embodiment, the copolymer has
27 all of the MWD, Intra-CD and Inter-CD characteristics des-
28 cribed above when incorporated in a lubricating oil or oil
29 additive concentrate composition. In current practice,
30 ethylene-propylene copolymer is most preferred. The pre-
31 ferred ethylene content of the copolymer, on a weight basis,
32 for use as a lube oil additive is about from 30% to 75%.

33 For lube oil additive applications, it is believed
34 that the copolymer could have a weight average molecular
35 weight as low as about 5,000. The preferred minimum is about
36 15,000, with about 50,000 being the most preferred minimum.
37 It is believed that the maximum weight average molecular

1 weight could be as high as about 500,000. The preferred
2 maximum is about 300,000, with about 250,000 being the most
3 preferred maximum.

4 Copolymers of this invention may be employed in
5 lubricating oils as viscosity index improvers or viscosity
6 modifiers in amounts varying broadly from about 0.001 to 49
7 wt.%. The proportions giving the best results will vary
8 somewhat according to the nature of the lubricating oil
9 basestock and the specific purpose for which the lubricant is
10 to serve in a given case. When used as lubricating oils for
11 diesel or gasoline engine crankcase lubricants, the polymer
12 concentrations are within the range of about 0.1 to 15.0 wt%
13 of the total composition which are amounts effective to
14 provide viscosity index improvements. Typically such poly-
15 meric additives are sold as oil additive concentrates wherein
16 the additive is present in amounts of about 5 to 50 wt%,
17 preferably 6 to 25 wt% based on the total amount of hydro-
18 carbon mineral oil diluent for the additive. The polymers of
19 this invention are typically used in lubricating oils based
20 on a hydrocarbon mineral oil having a viscosity of about 2-
21 40 centistokes (ASTM D-445) at 99°C, but lubricating oil
22 basestocks comprised of a mixture of a hydrocarbon mineral
23 oil and up to about 25 wt% of a synthetic lubricating oil such
24 as esters of dibasic acids and complex esters derived from
25 monobasic acids, polyglycols, dibasic acids and alcohols are
26 also considered suitable.

27 Finished lubricating oils containing the ethylene-
28 alpha-olefin polymers of the present invention will typi-
29 cally contain a number of other conventional additives in
30 amounts required to provide their normal attendant functions
31 and these include ashless dispersants, metal or over-based
32 metal detergent additives, zinc dihydrocarbyl dithiophos-
33 phate, anti-wear additives, anti-oxidants, pour depressants,
34 rust inhibitors, fuel economy or friction reducing additives
35 and the like.

36 The ashless dispersants include the polyalkenyl or
37 borated polyalkenyl succinimide where the alkenyl group is

1 derived from a C₃-C₄ olefin, especially polyisobutenyl hav-
2 ing a number average molecular weight of about 700 to 5,000.
3 Other well known dispersants include the oil soluble polyol
4 esters of hydrocarbon substituted succinic anhydride, e.g.,
5 polyisobutenyl succinic anhydride and the oil soluble oxaz-
6 zoline and lactone oxazoline dispersants derived from hydro-
7 carbon substituted succinic anhydride and di-substituted
8 amino alcohols. Lubricating oils typically contain about 0.5
9 to 5 wt.% of ashless dispersant.

10 The metal detergent additives suitable in the
11 oil are known in the art and include one or more members
12 selected from the group consisting of overbased oil-soluble
13 calcium, magnesium and barium phenates, sulfurized phenates,
14 and sulfonates especially the sulfonates of C₁₆-C₅₀ alkyl
15 substituted benzene or toluene sulfonic acids which have a
16 total base number of about 80 to 300. These overbased
17 materials may be used as the sole metal detergent additive or
18 in combination with the same additives in the neutral form but
19 the overall metal detergent additive combination should have
20 a basicity as represented by the foregoing total base number.
21 Preferably they are present in amounts of from about 0.5 to 8
22 wt.% with a mixture of overbased magnesium sulfurized phenate
23 and neutral calcium sulfurized phenate, obtained from C₈ to
24 C₁₂ alkyl phenols being especially useful.

25 The anti-wear additives useful are the oil-solu-
26 ble zinc dihydrocarbyldithiophosphate having a total of at
27 least 5 carbon atoms, preferably alkyl groups of C₄-C₈,
28 typically used in amounts of about 0.5-6% by weight.

29 Other suitable conventional viscosity index im-
30 provers, or viscosity modifiers, are the olefin polymers such
31 as other ethylene-propylene copolymers (e.g., those dis-
32 closed in the prior art as discussed above), polybutene,
33 hydrogenated polymers and copolymers and
34 terpolymers of styrene with isoprene and/or butadiene, poly-
35 mers of alkyl acrylates or alkyl methacrylates, copolymers of
36 alkyl methacrylates with N-vinyl pyrrolidone or dimethyl-

1 aminoalkyl methacrylate, post-grafted polymers of ethylene-
2 propylene with an active monomer such as maleic anhydride
3 which may be further reacted with alcohol or an alkylene
4 polyamine, styrene-maleic anhydride polymers post-reacted
5 with alcohols and amines and the like. These are used as
6 required to provide the viscosity range desired in the
7 finished oil, in accordance with known formulating tech-
8 niques.

9 Examples of suitable oxidation inhibitors are hin-
10 dered phenols, such as 2,6-ditertiary-butyl-paracresol, a-
11 mines, sulfurized phenols and alkyl phenothiazines; usually

12 a lubricating oil will contain about 0.01 to 3 weight percent
13 of oxidation inhibitor depending on its effectiveness.

14 Rust inhibitors are employed in very small pro-
15 portions such as about 0.1 to 1 weight percent with suitable
16 rust inhibitors being exemplified by C₉-C₃₀ aliphatic suc-
17 cinic acids or anhydrides such as dodecenyl succinic anhy-
18 dride.

19 Antifoam agents are typically the polysiloxane
20 silicone polymers present in amounts of about 0.01 to 1 weight
21 percent.

22 Pour point depressants are used generally in a-
23 mounts of from about 0.01 to about 10.0 wt.%, more typically
24 from about 0.01 to about 1 wt.%, for most mineral oil
25 basestocks of lubricating viscosity. Illustrative of pour
26 point depressants which are normally used in lubricating oil
27 compositions are polymers and copolymers of n-alkyl meth-
28 acrylate and n-alkyl acrylates, copolymers of di-n-alkyl
29 fumarate and vinyl acetate, alpha-olefin copolymers, alky-
30 lated naphthalenes, copolymers or terpolymers of alpha-
31 olefins and styrene and/or alkyl styrene, styrene dialkyl
32 maleic copolymers and the like.

33 As noted above, copolymer products made in
34 accordance with the present invention have excellent low
35 temperature properties which makes them suitable for lube
36 oil applications. Accordingly, lube oil compositions made

1 in accordance with the present invention preferably have
2 a Mini Rotary Viscosity (MRV) measurement in centipoises
3 (cps) at -25°C according to ASTM-D 3829 of less than
4 30,000. A more preferred MRV is less than 20,000, with
5 less than 10,000 being most preferred.

6 With reference again to processes for making co-
7 polymer in accordance with the present invention, it is
8 well known that certain combinations of vanadium and
9 aluminum compounds that can comprise the catalyst system
10 can cause branching and gelation during the polymerization
11 for polymers containing high levels of diene. To prevent
12 this from happening Lewis bases such as ammonia, tetra-
13 hydrofuran, pyridine, tributylamine, tetrahydrothiophene,
14 etc., can be added to the polymerization system using
15 techniques well known to those skilled in the art.

16 Example 1

17 In this example, an ethylene-propylene copolymer
18 was prepared in a conventional continuous flow stirred tank
19 reactor. Catalyst, monomers and solvent were fed to a 3 gallon
20 reactor at rates shown in the accompanying Table I. Hexane was
21 purified prior to use by passing over 4A molecular sieves
22 (Union Carbide, Linde Div. 4A 1/16" pellets) and silica gel
23 (W. R. Grace Co., Davison Chemical Div., PA-400 20-40 mesh) to
24 remove polar impurities which act as catalyst poisons. Gas-
25 eous ethylene and propylene were passed over hot (270°C) CuO
26 (Harshaw Chemical Co., CU1900 1/4" spheres) to remove oxygen
27 followed by mol sieve treatment for water removal and then were
28 combined with the hexane upstream of the reactor and passed
29 through a chiller which provided a low enough temperature to
30 completely dissolve the monomers in the hexane. Polymeriza-
31 tion temperature was controlled by allowing the cold feed to
32 absorb the heat of reaction generated by the polymerization.
33 The reactor outlet pressure was controlled at 413 kPa to ensure
34 dissolution of the monomers and a liquid filled reactor.

35 Catalyst solution was prepared by dissolving 37.4 g
36 of VCl_4 in 7 l of purified n-hexane. Cocatalyst consisted of
37 96.0 g $\text{Al}_2\text{Et}_3\text{Cl}_3$ in 7 l of n-hexane. These solutions were fed

1 to the reactor at rates shown in Table I. For the case of
2 catalyst premixing the two solutions were premixed at 0°C for
3 10 seconds prior to entry into the reactor.

4 Copolymer was deashed by contacting with aqueous
5 base and recovered by steam distillation of the diluent with
6 mill drying of the product to remove residual volatiles. The
7 product so prepared was analyzed for composition, composi-
8 tional distribution and molecular weight distribution using
9 the techniques discussed in the specification. Results were
10 as in Table I.

11 The copolymers were essentially compositionally ho-
12 mogeneous with heterogeneity $\pm 3\%$ about the average, i.e.
13 within experimental error.

14 These results indicate that for copolymer made in a
15 continuous flow stirred reactor the \bar{M}_w/\bar{M}_n was about 2 and the
16 Intra-CD was less than 5% ethylene. Catalyst premixing had no
17 effect on \bar{M}_w/\bar{M}_n or compositional distribution. Experiments
18 over a range of polymerization conditions with the same
19 catalyst system produced polymers of similar structure.

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Table I

	Example 1A	Example 1B
Reactor Inlet Temperature (°C)	-40	-35
Reactor Temperature (°C)	38	37.5
Reactor Feed Rates		
Hexane (kg/hr)	39.0	23.7
Ethene (g/hr)	1037	775
Propene (g/hr)	1404	1185
VC1 ₄ (g/hr)	5.41	2.56
Al ₂ Et ₃ Cl ₃ (g/hr)	17.4	13.2
Catalyst Premixing Temperature (°C)	Not premixed	0
Catalyst Premixing Time (sec)	Not premixed	10
Reactor Residence Time (min)	10.5	17.1
Rate of Polymerization (g/hr)	2256	1516
Catalyst Efficiency (g polymer/g V)	416	591
(\bar{M}_w) (a)	1.5×10^5	2.1×10^5
(\bar{M}_w/\bar{M}_n) (b)	2.1	1.9
(\bar{M}_z/\bar{M}_w) (a)	1.7	1.7
Average Composition (Ethylene wt.2) (c)	43	47
Compositional Distribution (d)		
	Inter-CD	Intra-CD
		High Ethylene
		Low Ethylene
Example 1A	+5 -1	0 0
Example 1B	+1 -3	+2 0

(a) Determined by GPC/LALLS using total scattered light intensity in 1,2,4 trichlorobenzene at 135°C, Chromatix R2X-6, specific refractive index increment $dn/dc = .104 \text{ g/cc}^{-1}$ (see specification)

(b) Determined from an elution time-molecular weight relationship as discussed in the specification, data precision ± 15

(c) Determined by ASTM D-3900 Method A. Data good to $\pm 2\%$ ethene.

(d) Composition determined on fractions which comprise 5-20% of the original polymer weight, hexane-isopropyl alcohol is solvent-non solvent pair.

(e) Inter-CD is determined as the difference between the maximum and minimum of the original polymer and the average composition.

(f) Chains fragmented to ca. 5% of their original molecular weight.

Intra-CD is determined as the difference in composition between the highest ethylene fractions of the original and fragmented chains and between the lowest such fractions.

1 Example 2

2 This example is seen to illustrate the importance
3 of reaction conditions in practicing methods in accordance
4 with the invention such as catalyst premixing for making
5 narrow MWD polymer with the desired Intra-CD. In examples
6 2(B.) and 2(C.) the catalyst components were premixed in
7 order to obtain rapid chain initiation. In example 2(A.) the
8 polymerization conditions were similar, but the catalyst
9 components were fed separately to the reactor inlet.

10 The polymerization reactor was a one-inch diameter
11 pipe equipped with Kenics static mixer elements along its
12 length. Monomers, hexane, catalyst, and cocatalyst were con-
13 tinuously fed to the reactor at one end and the copolymer
14 solution and unreacted monomers were withdrawn from the oth r
15 end. Monomers were purified and reactor temperature and
16 pressure was controlled as in Example 1.

17 A catalyst solution was prepared by dissolving 18.5
18 g of vanadium tetrachloride, VCl_4 , in 5.0 l of purified n-hex-
19 ane. The cocatalyst consisted of 142 g of ethyl aluminum
20 sesqui chloride, $\text{Al}_2\text{Et}_3\text{Cl}_3$, in 5.0 l of purified n-hexane. In
21 the case of catalyst premixing, the two solutions were pre-
22 mixed at a given temperature (as indicated in TABLE II) for
23 10 seconds prior to entry into the reactor.

24 Table II lists the feed rates for the monomers,
25 catalyst, and the residence time of examples 2(A.), (B.), and
26 (C.). Polymer was recovered and analyzed as in Example 1.

27 Figure 5 illustrates the polymer concentration-
28 residence time relationship, with concentration being
29 presented in terms of polymer concentration at residence time
30 t ($C_{\text{at residence time } t}$)/polymer concentration at final t
31 ($C_{\text{final } t}$) which exists at the end of the reactor. It is
32 evident that in example 2(B.) the maximum polymerization rate
33 occurs at about zero reaction time indicating fast initiation
34 of all the polymer chains. As a result, a very narrow MWD EPM
35 with (\bar{M}_w/\bar{M}_n) equal to 1.3 and (\bar{M}_z/\bar{M}_w) of 1.2 was produced
36 through a process in accordance with the present invention.

1 On the other hand, example 2(A.) shows that EPM with
2 \bar{M}_w/\bar{M}_n greater than 2.0 and \bar{M}_z/\bar{M}_w of 2.0 was obtained when the
3 proper conditions were not used. In this example, lack of
4 premixing of the catalyst components led to a reduced rate of
5 chain initiation and broadened MWD.

6 Samples of product were fractionated according to
7 the procedure of Example 1 and as disclosed in the specifica-
8 tion. Data appear in Table II.

9 Sample A, made without catalyst premixing, had a
10 broad Inter-CD typical of the prior art (e.g., Junghanns).
11 For samples B and C Inter-CD was much reduced as a result of
12 the premixing.

13 Intra-CD is shown as the difference between the
14 fractionation data on the fragmented and unfragmented sam-
15 ples. For sample B, the chains are shown to contain segments
16 of at least 6% ethylene higher than that isolatable on the
17 unfragmented material. The residual Inter-CD obscures the
18 analysis of Intra-CD. To make the analysis clearer, sample
19 C was first fractionated and then one fraction (the 3rd) was
20 refractionated showing it to be homogeneous with regard to
21 Inter-CD. Upon fragmentation a compositional dispersity as
22 large as the original whole polymer Inter-CD was obtained.
23 Thus, those chains must have had an Intra-CD of greater than
24 18%. The 2nd and 3rd fractions, which were similar, comprised
25 more than 70% of the original polymer showing that the Inter-
26 CD which obscured the Intra-CD was only due to a minor portion
27 of the whole polymer.

28 Since the fractionation procedure might depend on
29 the solvent non-solvent pair used, a second combination,
30 carbon tetrachloride-ethyl acetate was used on the sample C
31 whole polymer. This pair was also used in the prior art. It
32 is apparent from the data of Table II that hexane-isopropanol
33 separated the polymer more efficiently than CCl_4 -ethyl ace-
34 tate.

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Table II

	Example 2A	Example 2B	Example 2C
3 Reactor Inlet Temperature (°C)	-20	-10	-10
4 Reactor Outlet Temperature (°C)	-3	0	0
5 Reactor Feed Rates			
6 Hexane (kg/hr)	60.3	60.3	60.3
7 Ethene (kg/hr)	0.4	0.22	0.22
8 Propene (kg/hr)	3.2	2.0	2.0
9 VCl_4 (g/hr)	2.22	2.22	2.22
10 $\text{Al}_2\text{Et}_3\text{Cl}_3$ (g/hr)	20.5	17.0	17.0
11 Catalyst Premixing Temperature (°C)	—	0	+10
12 Catalyst Premixing Time (sec)	0	10	10
13 Reactor Residence Time (sec)	52	50	-35
14 Rate of Polymerization (g/hr)	874	503	426
15 Catalyst Efficiency (g polymer/g VCl_4)	394	227	192
16 (\bar{M}_w) (a)	2.1×10^5	1.4×10^5	9.5×10^4
17 (\bar{M}_w/\bar{M}_n) (a)	2.0	1.3	1.2
18 (\bar{M}_w/\bar{M}_n) (b)	2.70	1.3	1.2
19 Composition (ethene wt. %)(c)	42.4	39.1	41.4
20 Compositional Distribution(d)			
21	Original	Fragmented	(f) Intra CD(g)
22	max min max min Inter CD max min		
23 2A	55 25	— —	+13 —(e) —(e)
24 2B	45 32	51 32	-17 +6 0
25 2C	49 34	51 (39)	-7 +2 —(e)
26 2C 3rd cut refractionated	42 39	48 32	-7 +8 -10
27 2C CCl_4 -ethyl acetate	45 34	— —	— — —
28 (a) Determined by GPC/LALLS using total scattered light intensity in 1,2,4 tri-			
29 chlorobenzene at 135°C, Chromatix KMX-6, specific refractive index increment			
30 $dn/dc = .104 \text{ g/cc.}^{-1}$ (see specification)			
31 (b) Determined from an elution time-molecular weight relationship as discussed			
32 in the specification, data precision $\pm .15$			
33 (c) Determined by ASTM D-3900 Method A. Data good to $\pm 2\%$ ethene.			
34 (d) Composition determined on fractions which comprise 5-20% of the original			
35 polymer weight, hexane isopropyl alcohol is solvent-non solvent pair.			
36 (e) In these cases inter CD obscured intra CD so no increase in CD was shown			
37 on fragmentation.			
38 (f) Inter-CD is determined as the difference between the maximum and minimum			
39 of the original polymer and the average composition.			
40 (g) Chains fragmented to ca. 5% of their original molecular weight. Inter-CD			
41 is determined as the difference in composition between the highest ethylene			
42 fractions of the original and fragmented chains and between the lowest			
43 such fractions.			

1 Example 3

2 This example illustrates the use of additional mon-
3 omer feed downstream of the reactor inlet (multiple feed
4 points) to vary polymer composition and compositional distri-
5 bution while maintaining a narrow MWD. In example 3(B.), a
6 second hexane stream containing only ethylene was fed into the
7 reactor downstream of the inlet in addition to those feeds used
8 at the inlet. In example 3(A.), the polymerization conditions
9 were the same except there was no second ethylene feed. The
10 polymerization procedures of example 2(B.) were repeated. The
11 process conditions are listed in Table III.

12 The data listed in Table III show that the sample
13 made with an additional monomer feed downstream of the reactor
14 inlet had the same MWD as the one made with all the monomer feed
15 at the reactor inlet. This combined with the increases in
16 ethylene composition of the "2nd feed point" sample and the
17 molecular weight of the final sample in example 3(B.) indicate
18 that the monomers in the second feed had been added to the
19 growing polymer chains. Therefore, the Intra-CD of the final
20 product must be as shown schematically in Figure 6.

21 It is apparent that since the chains continue to grow
22 down the tube that a variety of structures can be produced by
23 using multiple feed points as noted in the specification.

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1	<u>Table III</u>		
2		Example 3B	Example 3A
3	Solvent Temperature (°C)		
4	Main Feed	-10	-10
5	Second Feed	0	—
6	Reactor Outlet Temperature (°C)	+3	0
7	Reactor Feed Rates		
8	Hexane (kg/hr)		
9	Main Feed	60.7	60.7
10	Second Feed	9.9	—
11	Ethylene (kg/hr)		
12	Main Feed	0.22	0.22
13	Second Feed	0.10	—
14	Propylene (kg/hr)	2.0	2.0
15	VCl ₄ (g/hr)	2.22	2.22
16	Al ₂ Et ₃ Cl ₃ (g/hr)	17.0	17.0
17	Reactor Residence Time (sec)		
18	Before the 2nd feed point	4	—
19	Overall	35	40
20	Premixing Temperature (°C)	0	0
21	Premixing Time (sec)	6	6
22	Rate of Polymerization (g/hr)	487	401
23	Catalyst Efficiency (g polymer/g VCl ₄)	219	181
24	(\bar{M}_w)	1.3×10^5	1.0×10^5
25	(\bar{M}_z/\bar{M}_w)		
26	(\bar{M}_w/\bar{M}_n)		
27	Composition (ethylene wt.%)		
28	Reactor sample taken right after		
29	the 2nd feed point	55.3	47.6
30	Final sample	45.4	41.0

1 Example 4

2 The comparison in this example illustrates that
3 narrow MWD EPM can also be produced in a tubular reactor
4 using the vanadium oxytrichloride (VOCl_3)-ethyl aluminum
5 sesqui chloride ($\text{Al}_2\text{Et}_3\text{Cl}_3$) system when the conditions
6 described earlier are used. In example 4(B.) the catalyst
7 components were premixed in order to obtain rapid chain ini-
8 tiation. In example 4(A.) the polymerization conditions
9 were the same, but the catalyst components were fed
10 separately to the reactor inlet. The polymerization pro-
11 cedures of example 2(A.) and 2(B.) were repeated. Table IV
12 lists the run conditions.

13 The data in Table IV indicate that premixing of the
14 catalyst components produces narrow MWD polymers ($\bar{M}_w/\bar{M}_n =$
15 1.8 and $\bar{M}_z/\bar{M}_w = 1.5$).

1

	Example 4A	Example 4B
3 Reactor Inlet Temperature (°C)	0	0
4 Reactor Outlet Temperature (°C)	7	12
5 Reactor Feed Rates		
6 Hexane (kg/hr)	60.2	61.1
7 Ethylene (kg/hr)	0.2	0.4
8 Propylene (kg/hr)	3.6	2.6
9 VOCl_3 (g/hr)	1.73	5.07
10 $\text{Al}_2\text{Et}_3\text{Cl}_3$ (g/hr)	7.44	54.2
11 Premixing Temperature (°C)	—	10
12 Premixing Time (sec)	—	6
13 Reactor Residence Time (sec)	52	37
14 Rate of Polymerization (g/hr)	685	359
15 Catalyst Efficiency (g polymer/g VOCl_3)	208	135
16 (\bar{M}_w)	2.8×10^5	3.3×10^5
17 (\bar{M}_w/\bar{M}_n)	2.7	1.5
18 (\bar{M}_w/\bar{M}_n)	2.7	1.8
19 Composition (ethylene wt.%)	40	49

1 Example 5

2
3 This example illustrates that narrow MWD ethylene-
4 propylene-diene copolymers (EPDM) can be produced in a tubular
5 reactor with premixing of the catalyst components. The
6 polymerization procedures of example 2(B.) were repeated,
7 except that a third monomer, 5-ethylidene-2-norbornene (ENB)
8 was also used. The feed rates to the reactor, premixing
9 conditions, and the residence time for example 5(A.) and 5(B.)
10 are listed in Table V. Also shown in Table V are the results
11 of a control polymerization (5C) made in a continuous flow
12 stirred tank reactor.

13 The copolymer produced was recovered and analyzed by
14 the procedures described in Example 1 above. In addition, the
15 ENB content was determined by refractive index measurement
16 (I. J. Gardner and G. Ver Strate, Rubber Chem. Tech. 46, 1019
17 (1973)). The molecular weight distribution, rate of poly-
18 merization and compositions are shown in Table V.

19 The data listed in Table V clearly demonstrate that
20 processes in accordance with the present invention also result
21 in very narrow MWD for EPDM.

22 Sample 5(B.) and 5(C.), a polymer made in a continuous
23 flow stirred reactor with similar composition and molecular
24 weight, were compounded in the following formulation:

25		
26	Polymer	100
27	High Abrasion Furnace	80
28	Black (PER)	
29	Oil (PHR)	50
30	ZnO (PHR)	2
31	Tetramethylthiuram Di-	1
32	sulfide (PER)	
33	2-Mercapto-1,2,4-benzothiazole	0.5
34	(PHR)	
35	S (PER)	1.5

1 The cured properties of these compounds are shown below:

2		<u>5B</u>	<u>Control (5C)</u>
3	Cure: 160°C/10'		
4	Tensile	1334	1276
5	Elong.	570	550
6	100% Mod.	244	261
7	200% Mod.	412	435
8	300% Mod.	600	618
9	400% Mod.	840	841
10	500% Mod.	1160	1102
11	Shore A	78	80
12		Monsanto: 160°C/60', 1° arc, 0-50 Range (a)	
13		(in-lb/dNm)	
14	ML (b)	2.8/3.2	4.0/4.5
15	ME (c)	37.2/42.0	35.0/39.6
16	ts2 (d)	2.8	3.0
17	t'90 (e)	22.2	18.5
18	Rate	7.9/8.9	5.9/6.7

19 (a) Monsanto Rheometer, Monsanto Company (Akron, OH)

20 (b) ML = Cure meter minimum torque; ASTM D2084-81

21 (c) ME = Cure meter maximum torque; ASTM D2084-81

22 (d) ts2 = Time (in minutes) to 2-point rise above minimum
23 torque; ASTM D2084-81

24 (e) t'90 = Time (in minutes) to reach 90% of maximum
25 torque rise above minimum; ASTM D2084-81.

26 These data show that the cure rate of the narrow
27 MWD polymer was greater than that for the continuous flow
28 stirred reactor control polymer even though
29 and ENB content were lower for the former. Thus, the
30 benefit of narrow MWD on cure rate is shown.

1

Table V

2	Example 5A	Example 5B	Example 5C
3 Reactor	Tubular	Tubular	Stirred Tank
4 Reactor Inlet Temperature (°C)	0	-20	
5 Reactor Outlet Temperature (°C)	20	-10	
6 Reactor Feed Rates			
7 Hexane (kg/hr)	60.9	60.9	
8 Ethylene (kg/hr)	0.65	0.20	
9 Propylene (kg/hr)	5.5	2.15	
10 Diene (kg/hr)	0.036	0.026	
11 VCl_4 (g/hr)	5.24	2.22	
12 $\text{Al}_2\text{Et}_3\text{Cl}_3$ (g/hr)	40.4	21.4	
13 Catalyst Premixing Temperature (°C)	0	-20	
14 Catalyst Premixing Time (sec)	6	10	
15 Reactor Residence Time (sec)	30	48	
16 Rate of Polymerization (g/hr)	1479	454	
17 Catalyst Efficiency (g polymer/g VCl_4)	282	205	
18 (\overline{M}_w)	1.3×10^5	1.2×10^5	1.6
19 $(\overline{M}_z/\overline{M}_w)$	1.37	1.30	4.
20 $(\overline{M}_w/\overline{M}_n)$	1.44	1.61	4.
21 Mooney Viscosity ML (1+8) 100°C	45	51	55
22 Composition			
23 Ethylene wt. %	39.3	39.3	49.
24 ENB wt. %	3.5	4.2	4.5
25 Cure Rate (dNm)	—	8.9	6.7

2 This example illustrates that narrow MWD EPM can be produced
3 in a tubular reactor with a different configuration when the critical
4 process conditions in accordance with the present invention are used.
5 The polymerization reactor consisted of 12 meters of a 3/8" tubing. The
6 experimental procedures of example 2(B.) were repeated. The process
7 conditions are listed in Table VI.

8 Data listed in Table VI show that this tubular reactor
9 produced polymer with an MWD as narrow as that of polymers made in the 1"
10 pipe used in the previous example.

TABLE VI

12	Reactor Inlet Temperature (°C)	-1
13	Reactor Outlet Temperature (°C)	30
14	Reactor Feed Rates	
15	Hexane (kg/hr)	31.1
16	Ethylene (kg/hr)	0.7
17	Propylene (kg/hr)	11
18	VCl_4 (g/hr)	8.27
19	$\text{Al}_2\text{Et}_3\text{Cl}_3$ (g/hr)	58.5
20	Reactor Residence Time (sec)	45
21	Catalyst Premixing Temperature (°C)	10
22	Catalyst Premixing Time (sec)	6
23	Rate of Polymerization (g/hr)	1832
24	Catalyst Efficiency (g polymer/g VCl_4)	222
25	(\bar{M}_w)	1.4×10^5
26	(\bar{M}_w/\bar{M}_n)	1.4
27	(\bar{M}_w/\bar{M}_n)	1.5
28	Composition (ethylene wt.%)	38

1 Examples 7-10

2 In these examples, polymers made as described in the previous
3 examples were dissolved in lubricating oil basestock and the
4 viscosity effects were evaluated. The narrow MWD and intra-
5 molecular compositional distribution of these polymers provide
6 improvements in MRV (Mini Rotary Viscosity) and SSI (Sonic
7 Shear Index).

8 MRV: This is a viscosity measurement in centipoises (cps) at
9 -25°C according to ASTM-D 3829 using the Mini-Rotary Viscometer
10 and is an industry accepted evaluation for the low temperature
11 pumpability of a lubricating oil.

12 T.E.: This represents Thickening Efficiency and is defined as
13 the ratio of the weight percent of a polyisobutylene (sold as
14 an oil solution by Exxon Chemical Company as Paratone N), having
15 a Staudinger molecular weight of 20,000, required to thicken a
16 solvent-extracted neutral mineral lubricating oil, having a
17 viscosity of 150 SUS at 37.8°C., a viscosity index of 105 and
18 an ASTM pour point of 0°F., (Solvent 150 Neutral) to a viscosity
19 of 12.3 centistokes at 98.9°C., to the weight percent of a test
20 copolymer required to thicken the same oil to the same viscosity
21 at the same temperature.

22 SSI: This value is Shear Stability Index and measures the
23 stability of polymers used as V.I. improvers in motor oils
24 subjected to high shear rates. In this method the sample under
25 test is blended with a typical basestock to a viscosity increase
26 at 210°F of 7.0 \pm 5 centistokes. Two portions of the blend are
27 successively subjected to sonic shearing forces at a specific

1 power input and a constant temperature for 15 minutes.
 2 Viscosities are determined on the blends both before and
 3 after the treatment; the decrease in viscosity after the
 4 treatment is a measure of the molecular breakdown of the
 5 polymer under test. A series of standard samples is used
 6 as a reference to establish the correct value for the sam-
 7 ple under test. The corrected value is reported as the
 8 SSI which is the percent sonic breakdown to the nearest
 9 1%.

10 In these tests, a Raytheon Model DF 101, 200
 11 watt, 10 kilocycle sonic oscillator was used, the temper-
 12 ature was 37 \pm 4°C, power input is 0.75 ampere, time of
 13 test is 15.0 minutes \pm 10 seconds.

14 Example 7

15 In this example, polymers made as described in Examples
 16 1 and 2 were dissolved in lubricating oil to provide a
 17 kinematic viscosity of 13.5 centistokes at 100°C (ASTM
 18 D445) SSI was measured in Solvent 150 Neutral basestock
 19 (31 cs. min at 100°F, pour point of 50°F and broad wax
 20 distribution). MRV was measured in a Mid-Continent base-
 21 stock being a mixture of Solvent 100 Neutral (20 cs. min
 22 at 100°F) and Solvent 250 Neutral (55 cs. min at 100°F)
 23 and having a narrow (C₂₄-C₃₆) wax distribution and contain-
 24 ing 0.2 wt% vinyl acetate fumarate pour depressant (Para-
 25 flow 442, Exxon Chemical Co.).

26 Results are tabulated below:

27	28 <u>Oil Containing</u>		29 <u>Shear Stability</u>		30 <u>Pumpability</u>
	28 Copolymer as	29 Ethylene	29 Thickening	29 SSI	30 MRV @ -25°C cps
30	30 Described In:	30 wt%	30 Efficiency	30 % Loss	
31	Example 1	42	2.8	28	32,500
32	Example 2A	42	3.6	44	270,000
33	Example 2B	39	2.7	18	25,000
34	Example 2C	41	2.06	8	20,000

1 These data clearly show the improvements in SSI and MRV
2 possible with the polymers of the present invention.
3 Example 2B outperformed Example 1 in SSI at the same TE.
4 Both Examples 2B and 2C, made with premixed catalyst, out-
5 performed Example 1 (made as in Ex. 1) from the backmixed
6 reactor, and Example 2A, made with no premixing and having
7 the broad inter CD.

8 Example 8

9 In this example it is shown that the polymer of Example 3,
10 which was made with multiple ethylene feeds and which re-
11 tained its narrow MWD even with a second ethylene feed,
12 has good shear stability.

13	<u>Sample</u>	<u>TE</u>	<u>SSI & Loss</u>
14	Example 2B	2.7	18
15	Example 3B	2.6	14.5

16 The shear stability of 3B was equivalent to the polymer
17 made with the single feed. Thus, it is possible to tailor
18 compositional distribution without significantly affect-
19 ing MWD and SSI.

20 Example 9

21 In this example it is shown that the premixing of the VOCl_3
22 catalyst components of Example 4, which effected a narrow-
23 ing of MWD, permits a much higher TE polymer to be em-
24 ployed with the same SSI, as shown in Table 9.

25 Table 9

26	<u>Sample</u>	<u>TE</u>	<u>SSI & Loss</u>
27	Example 4A	3.8	52
28	Example 4B	4.9	53

1 It should be noted, however, that a polymer of the same
2 TE as the polymer of Example 4A, when made with premixing
3 exhibits much better SSI than the Example 4A.

4 Example 10

5 This example demonstrates a terpolymer in accordance
6 with this invention exhibits the same viscosity improve-
7 ments. A terpolymer sample was prepared as in Example
8 5(A). This sample was tested for SSI and MRV. Sample
9 analysis and results appear in Table 10.

10

Table 10

11	<u>Sample</u>	<u>Ethylene wt%</u>	<u>PNB wt%</u>	<u>TE</u>	<u>MRV</u>	<u>SSI, % Loss</u>
12	Example 10A	39.3	3.5	2.5	33,000	29

CLAIMS:

1. Copolymer of ethylene and at least one other alpha-olefin monomer, said copolymer having an average ethylene composition and comprising intramolecularly heterogeneous copolymer chains wherein at least two portions of an individual intramolecularly heterogeneous chain, each portion comprising at least 5 weight percent of said chain, differ in composition from one another by at least 5 weight percent ethylene, wherein said copolymer has an intermolecular compositional dispersity such that 95 weight percent of said copolymer chains have a composition 15 weight percent or less different from said average ethylene composition, and wherein said copolymer has a MWD characterized by at least one of a ratio of \bar{M}_w/\bar{M}_n of less than 2 and a ratio of \bar{M}_z/\bar{M}_w of less than 1.8.

2. A copolymer according to Claim 1, wherein said intermolecular compositional dispersity of said copolymer is such that 95 weight percent of said copolymer chains have a composition 13% or less different from said average ethylene composition.

3. A copolymer according to Claim 1, wherein said intermolecular compositional dispersity of said copolymer is such that 95 weight percent of said copolymer chains have a composition 10% or less different from said average ethylene composition.

4. A copolymer according to Claim 1, wherein said at least two portions of an individual chain differ in composition from one another by at least 10 weight percent ethylene.

5. A copolymer according to Claim 1, wherein said at least two portions of an individual chain differ in composition from one another by at least 20 weight percent ethylene.

6. A copolymer according to Claim 1, wherein said at least two portions of an individual chain differ in composition from one another by at least 40 weight percent ethylene.

7. A copolymer according to Claim 1, which has a MWD characterized by at least one of a ratio of \bar{M}_w/\bar{M}_n of less than about 1.6 and a ratio of \bar{M}_z/\bar{M}_w of less than about 1.5.

8. A copolymer according to Claim 1, which has a MWD characterized by both a ratio of \bar{M}_w/\bar{M}_n of less than about 1.6 and a ratio of \bar{M}_z/\bar{M}_w of less than about 1.5.

9. A copolymer according to Claim 1, which has a MWD characterized by at least one of a ratio of \bar{M}_w/\bar{M}_n of less than about 1.4 and a ratio of \bar{M}_z/\bar{M}_w of less than about 1.3.

10. A copolymer according to Claim 1, which has a MWD characterized by both of a ratio of \bar{M}_w/\bar{M}_n of less than about 1.4 and a ratio of \bar{M}_z/\bar{M}_w of less than about 1.3.

11. A copolymer according to Claim 7 or 8, wherein said intermolecular compositional dispersity of said copolymer is such that 95 weight percent of said copolymer chains have a composition 13% or less different from said average ethylene composition, and wherein said at least two portions of an individual chain differ in composition from one another by at least 10 weight percent ethylene.

12. A copolymer according to Claim 9 or 10, wherein said intermolecular compositional dispersity of said copolymer is such that 95 weight percent of said copolymer chains have a composition 10% or less different from said average ethylene composition, and wherein said at least two portions of an individual chain differ in composition from one another by at least 20 weight percent ethylene.

13. A copolymer according to Claim 11, wherein said at least two portions of an individual chain differ in composition from one another by at least 40 weight percent ethylene.

14. A copolymer according to Claim 12, wherein said at least two portions of an individual chain differ in composition from one another by at least 40 weight percent ethylene.

15. A copolymer according to Claim 1, having a total maximum ethylene content of about 90% on a weight basis.

16. A copolymer according to Claim 1, having a total maximum ethylene content of about 85% on a weight basis.

17. A copolymer according to Claim 15 or 16, wherein said intermolecular compositional dispersity of said copolymer is such that 95 weight percent of said copolymer chains have a composition 13% or less different from said average ethylene composition.

18. A copolymer according to Claim 15 or 16, wherein said intermolecular compositional dispersity of said copolymer is such that 95 weight percent of said copolymer chains have a composition 10% or less different from said average ethylene composition.

19. A copolymer according to Claim 15 or 16, wherein said at least two portions of an individual chain differ in composition from one another by at least 10 weight percent ethylene.

20. A copolymer according to Claim 15 or 16, wherein said at least two portions of an individual chain differ in composition from one another by at least 20 weight percent ethylene.

21. A copolymer according to Claim 15 or 16, wherein said at least two portions of an individual chain differ in composition from one another by at least 40 weight percent ethylene.

22. A copolymer according to Claim 15 or 16, which has a MWD characterized by at least one of a ratio of \bar{M}_w/\bar{M}_n of less than about 1.6 and a ratio of \bar{M}_z/\bar{M}_w of less than about 1.5.

23. A copolymer according to Claim 15 or 16, which has a MWD characterized by both a ratio of \bar{M}_w/\bar{M}_n of less than about 1.6 and a ratio of \bar{M}_z/\bar{M}_w of less than about 1.5.

24. A copolymer according to Claim 15 or 16, which has a MWD characterized by at least one of a ratio of \bar{M}_w/\bar{M}_n of less than about 1.4 and a ratio of \bar{M}_z/\bar{M}_w of less than about 1.3.

25. A copolymer according to Claim 15 or 16, which has a MWD characterized by both of a ratio of \bar{M}_w/\bar{M}_n of less than about 1.4 and a ratio of \bar{M}_z/\bar{M}_w of less than about 1.3.

26. A copolymer according to Claim 22, wherein said intermolecular compositional dispersity of said copolymer is such that 95 weight percent of said copolymer chains have a composition 1% or less different from said average ethylene composition, and wherein said at least two

portions of an individual chain differ in composition from one another by at least 10 weight percent ethylene.

27. A copolymer according to Claim 24, wherein said intermolecular compositional dispersity of said copolymer is such that 95 weight percent of said copolymer chains have a composition 10% or less different from said average ethylene composition, and wherein said at least two portions of an individual chain differ in composition from one another by at least 20 weight percent ethylene.

28. A copolymer according to Claim 26, wherein said at least two portions of an individual chain differ in composition from one another by at least 40 weight percent ethylene.

29. A copolymer according to Claim 27, wherein said at least two portions of an individual chain differ in composition from one another by at least 40 weight percent ethylene.

30. A copolymer according to Claim 1, 15 or 16, having a total ethylene content of greater than about 25% on a weight basis.

31. A copolymer according to Claim 1, 15 or 16, further comprising diene.

32. A copolymer according to Claim 26, further comprising diene.

33. A copolymer according to Claim 32, wherein the total ethylene content is about 30% to 75% on a weight basis.

34. A copolymer according to Claim 11 which is comprised of ethylene, propylene and ENB.

35. A copolymer according to Claim 1 which is cured.
36. A copolymer according to Claim 11 which is cured.
37. A copolymer according to Claim 1, which has a weight average molecular weight of about 2,000 to 12,600,000.
38. A copolymer according to Claim 1, which has a weight average molecular weight of about 10,000 to 1,000,000.
39. A copolymer according to Claim 1, which has a weight average molecular weight of about 20,000 to 750,000.
40. In a polymerization process for producing copolymer in the form of copolymer chains, from a reaction mixture comprised of catalyst, ethylene, and at least one other alpha-olefin monomer, the improvement which comprises conducting the polymerization:
- (a) in at least one mix-free reactor,
 - (b) with essentially one active catalyst species,
 - (c) using at least one reaction mixture which is essentially transfer agent-free, and
 - (d) in such a manner and under conditions sufficient to initiate propagation of essentially all copolymer chains simultaneously, wherein the copolymer chains produced are dispersed with the reaction mixture.
41. A process according to Claim 40, wherein the catalyst comprises hydrocarbon-soluble vanadium compound and organo-aluminum compound which react to form essentially one active catalyst species, at least one of the vanadium compound and organo-aluminum compound containing a valence-bonded halogen.

42. A process according to Claim 40 or 41, wherein the inlet temperature of the reaction mixture is about -50°C to 150°C .

43. A process according to Claim 42, wherein the maximum outlet temperature of the reaction mixture is about 200°C .

44. A process according to Claim 43, wherein the catalyst components are premixed, and wherein the polymerization is a solution polymerization.

45. A process according to Claim 44, wherein the catalyst components are aged for at least about .5 seconds.

46. A process according to Claim 41, wherein the mole ratio of aluminum to vanadium in the catalyst is about 2 to 25.

47. A process according to Claim 44, wherein the reaction mixture leaving the reactor has a copolymer concentration of about 3 to 15% on a weight of copolymer per weight of solvent basis.

48. A process according to Claim 40, wherein the catalyst comprises a Ziegler catalyst.

49. A process according to Claim 42, wherein the maximum outlet temperature of the reaction mixture is about 50°C .

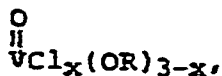
50. A process according to Claim 47, wherein the catalyst comprises components that are premixed and then aged for about 1 to 50 seconds.

51. A process according to Claim 47, wherein the mole ratio of aluminum to vanadium in the catalyst is about 4 to 15.

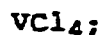
52. A process according to Claim 51, wherein the polymerization is conducted in a solvent for the reaction mixture, and wherein the reaction mixture leaving the reactor has a copolymer concentration of about 3% to 10% on a weight of polymer per weight of solvent basis.

53. A process according to Claim 41, wherein the catalyst comprises:

(a) hydrocarbon-soluble vanadium compound selected from the group consisting of:



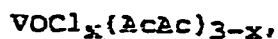
where $x=0-3$ and $R=\text{hydrocarbon radical}$;



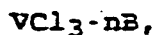
where $\text{AcAc}=\text{acetyl acetate}$



where $\text{AcAc}=\text{acetyl acetate}$



where $x=1$ or 2 and $\text{AcAc}=\text{acetyl acetate}$; and



where $n=2-3$ and $\text{B}=\text{Lewis base capable of forming hydrocarbon-soluble complexes with } \text{VCl}_3$; and

(b) organo-aluminum compound selected from the group consisting of:

AlR_3

AlR_2Cl ,

$Al_2R_3Cl_3$,

$AlRCl_2$,

$AlR'RCl$,

$Al(OR')R_2$,

$R_2Al-OAlR_2$, and

AlR_2I ,

where R and R' are hydrocarbon radicals

54. A process according to Claim 41, wherein the catalyst comprises VCl_4 and $Al_2R_3Cl_3$.

55. A process according to Claim 43, wherein the maximum outlet temperature of the reaction mixture is about 70°C.

56. A process according to Claim 55, wherein the polymerization is adiabatic.

57. A process according to Claim 56, wherein the catalyst comprises one active species which provides for at least 65% of the total copolymer produced.

58. A process according to Claim 57, which is continuous and is conducted in hexane solvent.

59. A process according to Claim 40, wherein said copolymer product is cured.

60. A process according to Claim 40, wherein said polymerization is conducted in at least one tubular reactor.

61. A process according to Claim 60, wherein said reaction mixture further comprises diene, and wherein at least one of said ethylene, other alpha-olefin monomer and diene are fed to said tubular reactor at multiple feed sites.

62. A process according to Claim 40, wherein said copolymer product is blended with basestock lubricating oil.

63. A process according to Claim 62, wherein said copolymer product is blended with the basestock lubricating oil in an amount of from about .001 to 49 wt. %.

64. A process according to Claim 40, wherein said copolymer product is blended with hydrocarbon mineral oil diluent in an amount of from about 5 to 50 wt. %.

65. A lubricating oil composition comprising a major amount of basestock lubricating oil, of lubricating viscosity, containing an effective amount of a viscosity index improver being a copolymer of ethylene and at least one other alpha-olefin monomer, wherein said copolymer has a MWD characterized by at least one of a ratio of \bar{M}_w/\bar{M}_n of less than 2 and a ratio of \bar{M}_z/\bar{M}_w of less than 1.8.

66. A lubricating oil composition according to Claim 65, wherein said copolymer has a total maximum ethylene content of about 90% on a weight basis.

67. A lubricating oil composition according to Claim 65 or 66, wherein said copolymer has a MWD characterized by at least one of a ratio of \bar{M}_w/\bar{M}_n of less than about 1.6 and a ratio of \bar{M}_z/\bar{M}_w of less than about 1.5.

68. A lubricating oil composition according to Claim 65 or 66, wherein said copolymer has a MWD characterized by at least one of a ratio of \bar{M}_w/\bar{M}_n of less than about 1.4 and a ratio of \bar{M}_z/\bar{M}_w of less than about 1.3.

69. A lubricating oil composition according to Claim 65 or 66, wherein said copolymer comprises intramolecularly heterogeneous chains wherein at least two portions of an individual intramolecularly heterogeneous chain, each portion comprising at least 5 weight percent of said chain, differ in composition from one another by at least 5 weight percent ethylene.

70. A lubricating oil composition according to Claim 65 or 66, wherein said copolymer has an intermolecular compositional dispersity such that 95 weight percent of said copolymer chains have a composition 15 weight percent or less different from the average ethylene composition of said copolymer.

71. A lubricating oil composition according to Claim 69, wherein said portions differ in composition by at least 10 weight percent ethylene.

72. A lubricating oil composition according to Claim 70, wherein said intermolecular compositional dispersity of said copolymer is such that 95 weight percent of said copolymer chains have a composition 13% or less different from said average ethylene composition.

73. A lubricating oil composition according to Claim 65, containing from about .001 to 49 wt.% of said copolymer.

74. A lubricating oil composition according to Claim 65, wherein said copolymer has a weight average molecular weight of about 5,000 to 500,000.

75. A lubricating oil composition according to Claim 71, wherein said copolymer has a MWD characterized by at least one of a ratio of \bar{M}_w/\bar{M}_n of less than about 1.6 and a ratio of \bar{M}_z/\bar{M}_w of less than about 1.5, and wherein said copolymer has an intermolecular compositional dispersity such that 95 weight percent of said copolymer chains have a composition 13% or less different from said average ethylene composition.

76. A lubricating oil composition according to Claim 75, wherein said intermolecular compositional dispersity is such that 95 weight percent of said copolymer chains have a composition 10% or less different from said average ethylene composition.

77. A lubricating oil composition according to Claim 71, wherein said copolymer has a MWD characterized by at least one of a ratio of \bar{M}_w/\bar{M}_n of less than about 1.4 and a ratio of \bar{M}_z/\bar{M}_w of less than about 1.3., and wherein said copolymer has an intermolecular compositional dispersity such that 95 weight percent of said copolymer chains have a composition 13% or less different from said average ethylene composition.

78. A lubricating oil composition according to Claim 77, wherein said intermolecular compositional dispersity is such that 95 weight percent of said copolymer chains have a composition 10% or less different from said average ethylene composition.

79. A lubricating oil composition according to Claim 74, wherein said weight average molecular weight is about 15,000 to 300,000.

80. A lubricating oil composition according to Claim 74, wherein said weight average molecular weight is about 50,000 to 250,000.

81. A lubricating oil composition according to Claim 65, wherein said copolymer comprises ethylene and propylene.

82. A lubricating oil composition according to Claim 81, wherein said copolymer further comprises diene.

83. A lubricating oil composition according to Claim 82, wherein said diene is ENB.

84. A lubricating oil composition according to Claim 65, having an MRV of less than 30,000.

85. A lubricating oil composition according to Claim 65, having an MRV of less than 20,000.

86. A lubricating oil composition according to Claim 65, having an MRV of less than 10,000.

87. An oil additive concentrate composition comprising hydrocarbon mineral oil diluent and about 5 to 50 wt.% based on the total amount of hydrocarbon mineral oil diluent of a copolymer of ethylene and at least one other alpha-olefin monomer, wherein said copolymer has a MWD characterized by at least one of a ratio of \bar{M}_w/\bar{M}_n of less than 2 and a ratio of \bar{M}_z/\bar{M}_w of less than 1.8.

88. An oil additive concentrate composition according to Claim 87, wherein said copolymer comprises intramolecularly heterogeneous chains wherein at least two portions of an individual intramolecularly heterogeneous chain, each portion comprising at least 5 weight percent of said chain, differ in composition from one another by at least 5 weight percent ethylene.

89. An oil additive concentrate composition according to Claim 87 or 88, wherein said copolymer has an intermolecular compositional dispersity such that 95 weight percent of said copolymer chains have a composition 15 weight percent or less different from the average ethylene composition of said copolymer.

90. An oil additive concentrate composition according to Claim 88, wherein said portions differ in composition by at least 10 weight percent ethylene.

91. An oil additive concentrate composition according to Claim 89, wherein said intermolecular compositional dispersity of said copolymer is such that 95 weight percent of said copolymer chains have a composition 13% or less different from said average ethylene composition.

92. An oil additive concentrate composition according to Claim 91, wherein said copolymer has a weight average molecular weight of about 5,000 to 500,000.

93. An oil additive concentrate composition according to Claim 92, wherein said weight average molecular weight is about 15,000 to 300,000.

94. An oil additive concentrate composition according to Claim 93, wherein said weight average molecular weight is about 50,000 to 250,000.

95. An oil additive concentrate composition according to Claim 94, wherein said copolymer comprises ethylene and propylene.

96. An oil additive concentrate composition according to Claim 87, wherein said copolymer has a total maximum ethylene content of about 90% on a weight basis.

97. An oil additive concentrate composition according to Claim 87 or 96, wherein said copolymer has a MWD characterized by at least one of a ratio of \bar{M}_w/\bar{M}_n of less than about 1.6 and a ratio of \bar{M}_z/\bar{M}_w of less than about 1.5.

98. An oil additive concentrate composition according to Claim 87 or 96, wherein said copolymer has a MWD characterized by at least one of a ratio of \bar{M}_w/\bar{M}_n of less than about 1.4 and a ratio of \bar{M}_z/\bar{M}_w of less than about 1.3.

99. An oil additive concentrate composition according to Claim 88, wherein said portions differ in composition by at least 10 weight percent ethylene.

100. An oil additive concentrate composition according to Claim 88, wherein said copolymer has a MWD characterized by at least one of a ratio of \bar{M}_w/\bar{M}_n of less than about 1.6 and a ratio of \bar{M}_z/\bar{M}_w of less than about 1.5, and wherein said copolymer has an intermolecular compositional dispersity such that 95 weight percent of said copolymer chains have a composition 13% or less different from said average ethylene composition.

101. An oil additive concentrate composition according to Claim 100, wherein said intermolecular compositional dispersity is such that 95 weight percent of said copolymer chains have a composition 10% or less different from said average ethylene composition.

102. An oil additive concentrate composition according to Claim 88, wherein said copolymer has a MWD characterized by at least one of a ratio of \bar{M}_w/\bar{M}_n of less

than about 1.4 and a ratio of \bar{M}_z/\bar{M}_w of less than about 1.3, and wherein said copolymer has an intermolecular compositional dispersity such that 95 weight percent of said copolymer chains have a composition 13% or less different from said average ethylene composition.

103. An oil additive concentrate composition according to Claim 102, wherein said intermolecular compositional dispersity is such that 95 weight percent of said copolymer chains have a composition 10% or less different from said average ethylene composition.

104. A lubricating oil composition comprising a major amount of basestock lubricating oil of lubricating viscosity containing an effective amount of a viscosity index improver being a copolymer of ethylene and at least one other alpha-olefin monomer produced in a mix-free reactor and blended in an effective amount with the basestock lubricating oil.

105. A lubricating oil composition according to Claim 104, wherein the basestock lubricating oil is mineral oil and the copolymer comprises copolymer of ethylene and propylene.

106. An oil additive concentrate composition comprising copolymer of ethylene and at least one other alpha-olefin produced in a mix-free reactor and blended with hydrocarbon mineral oil diluent in an amount of about 5 to 50 wt.% based on hydrocarbon mineral oil diluent.

107. An oil additive concentrate composition according to Claim 106, wherein the copolymer comprises copolymer of ethylene and propylene.

108. The use of a copolymer of ethylene and at least one other alpha-olefin monomer, which copolymer has a MWD characterised by a ratio of \bar{M}_w/\bar{M}_n of less than 2 and/or a ratio of \bar{M}_z/\bar{M}_w of less than 1.8, as a viscosity index improver for lubricating oil compositions.

109. The use according to Claim 108 wherein the copolymer has an average ethylene composition and comprises intramolecularly heterogeneous copolymer chains wherein at least two portions of an individual intramolecularly heterogeneous chain, each portion comprising at least 5 weight percent of said chain, differ in composition from one another by at least 5 weight percent ethylene, and/or wherein said copolymer has an intermolecular compositional dispersity such that 95 weight percent of said copolymer chains have a composition 15 weight percent or less different from said average ethylene composition.

110. The use according to Claim 108 or 109 wherein the lubricating oil composition additionally includes one or more additives selected from other viscosity index improvers or modifiers, dispersants, metal detergent additives, antiwear additives, oxidation inhibitors, rust inhibitors, antifoam agents and pour point depressants.

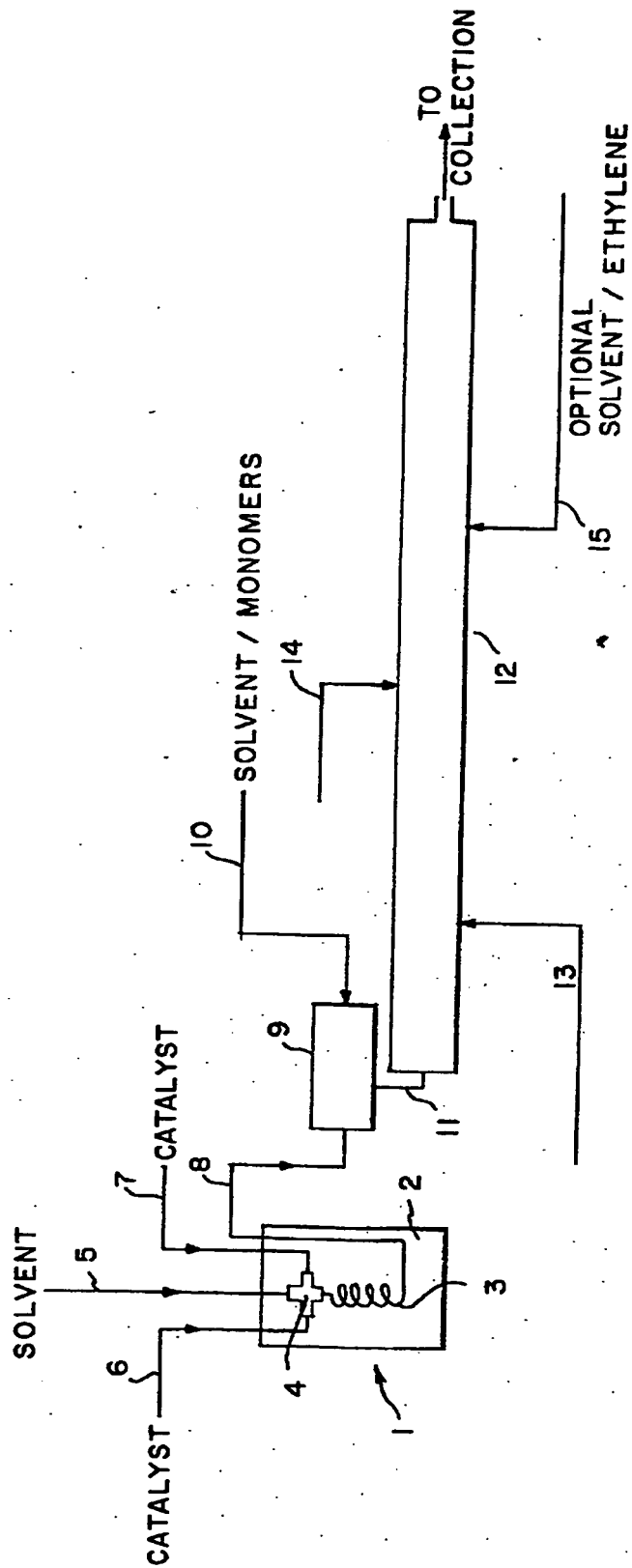


FIG. 1

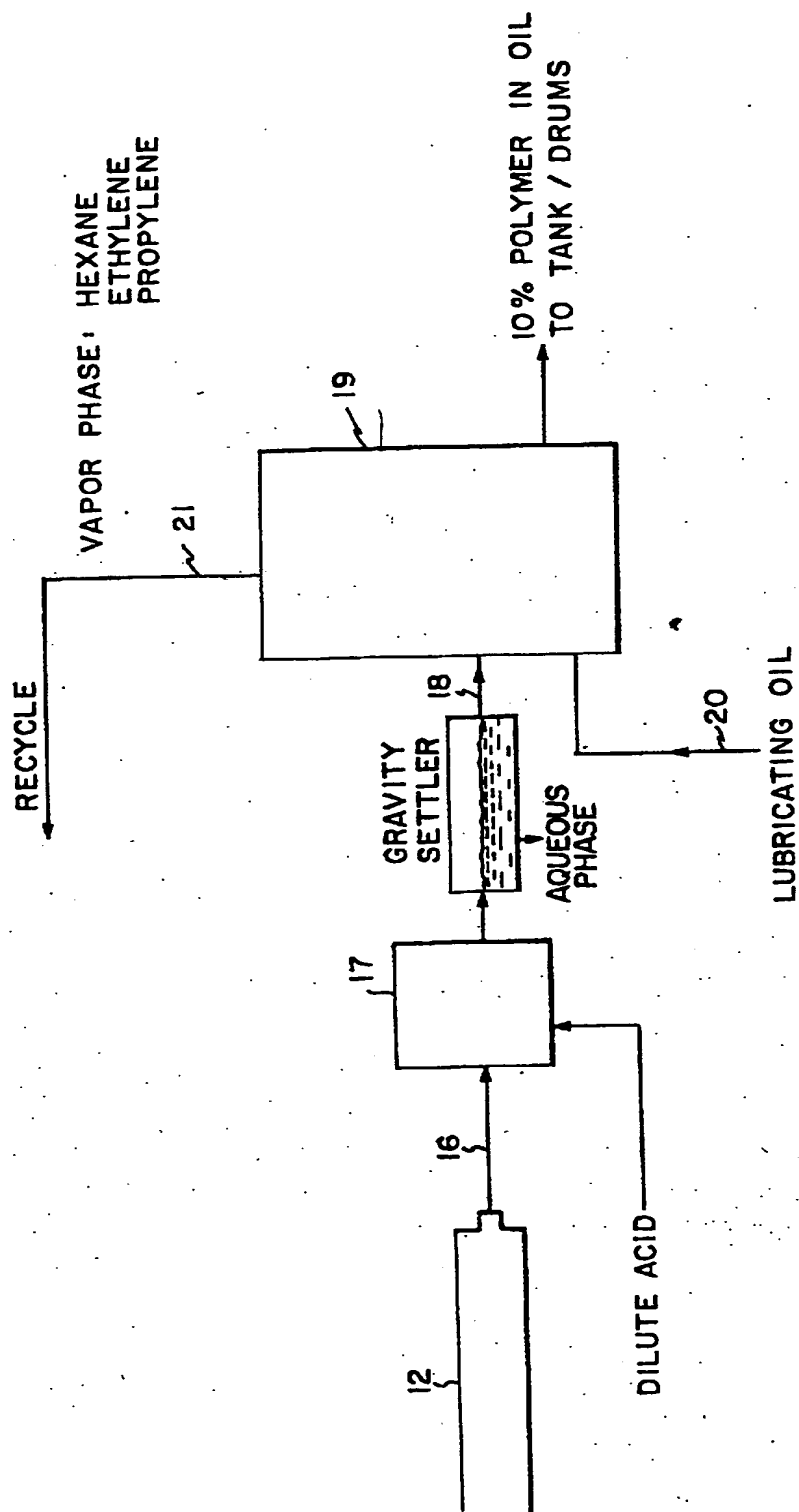


FIG. 2

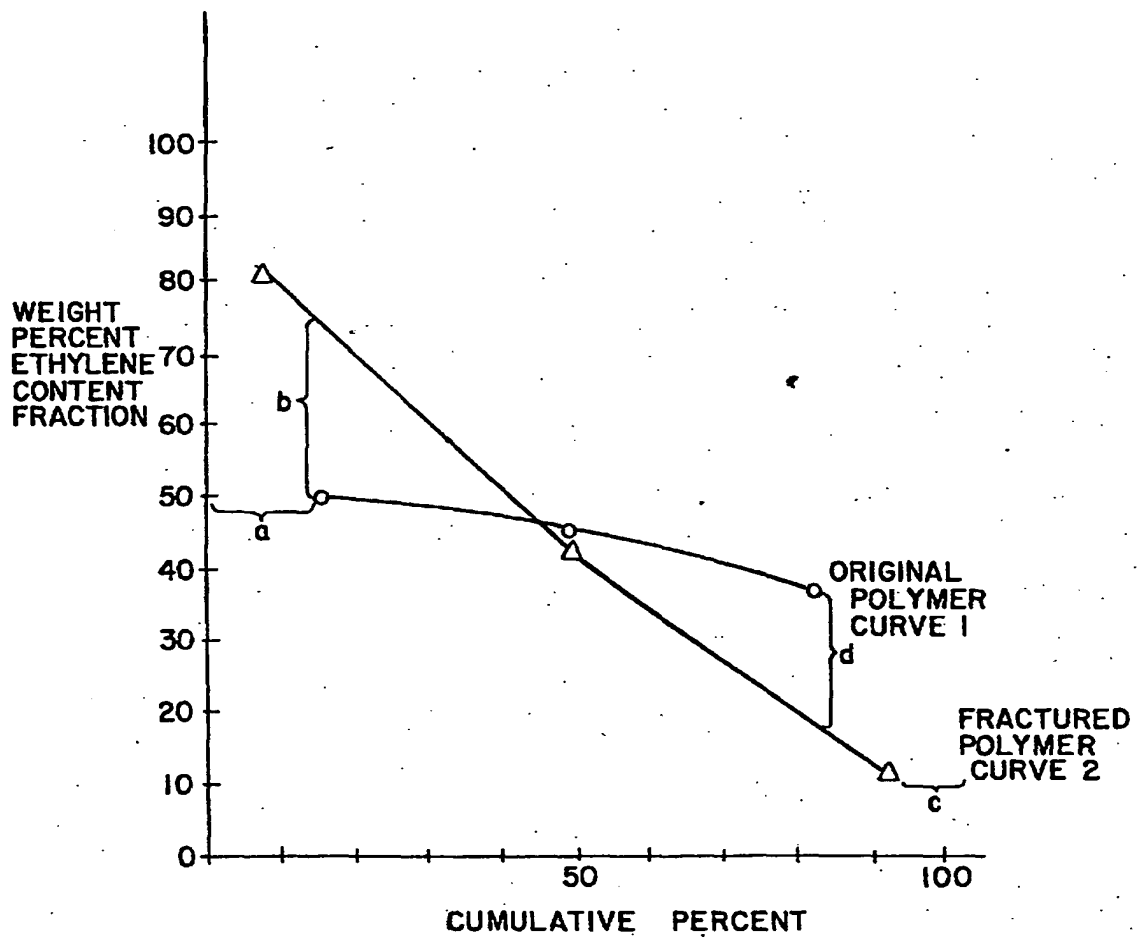
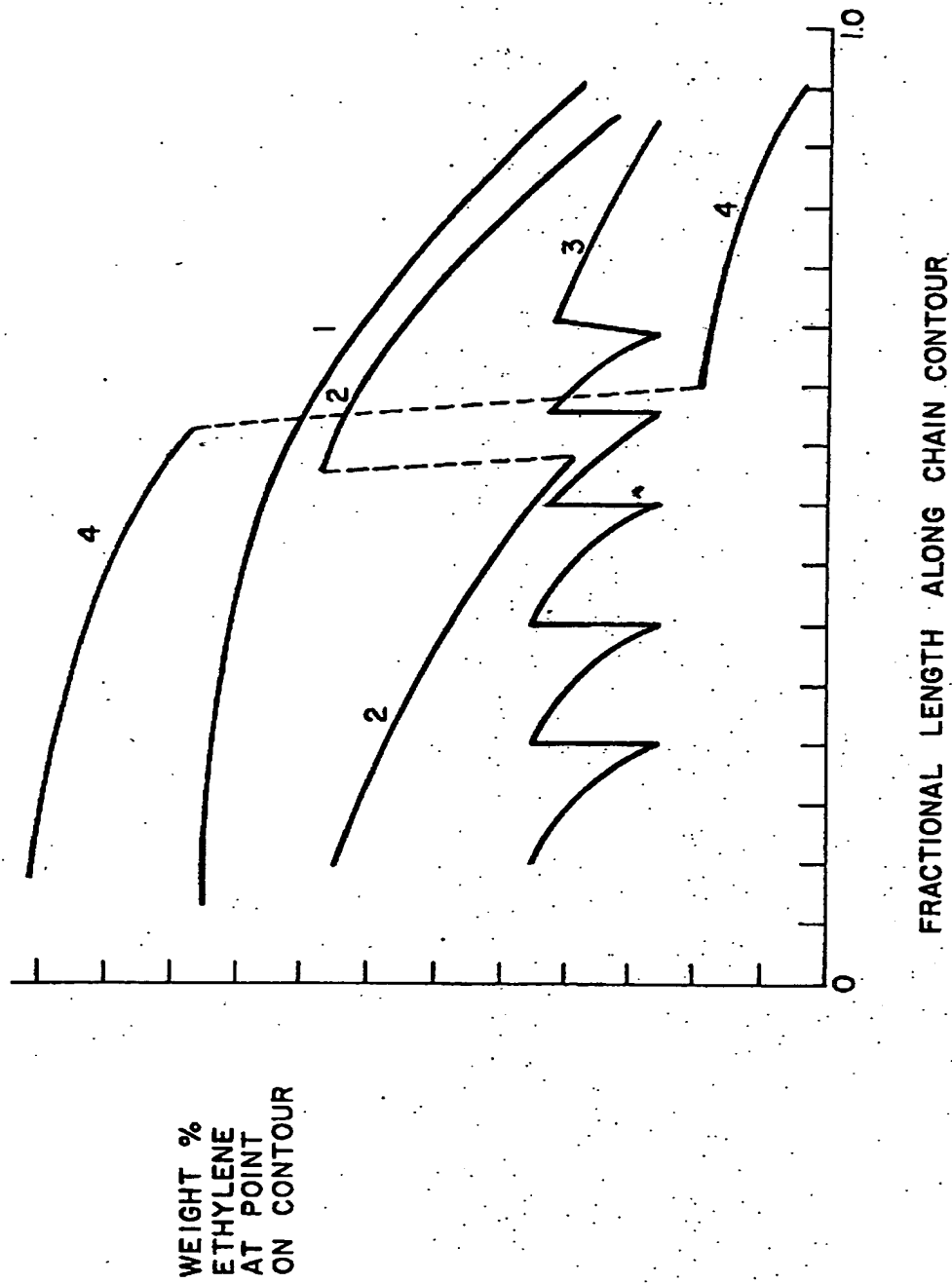


FIG. 3

FIG. 4



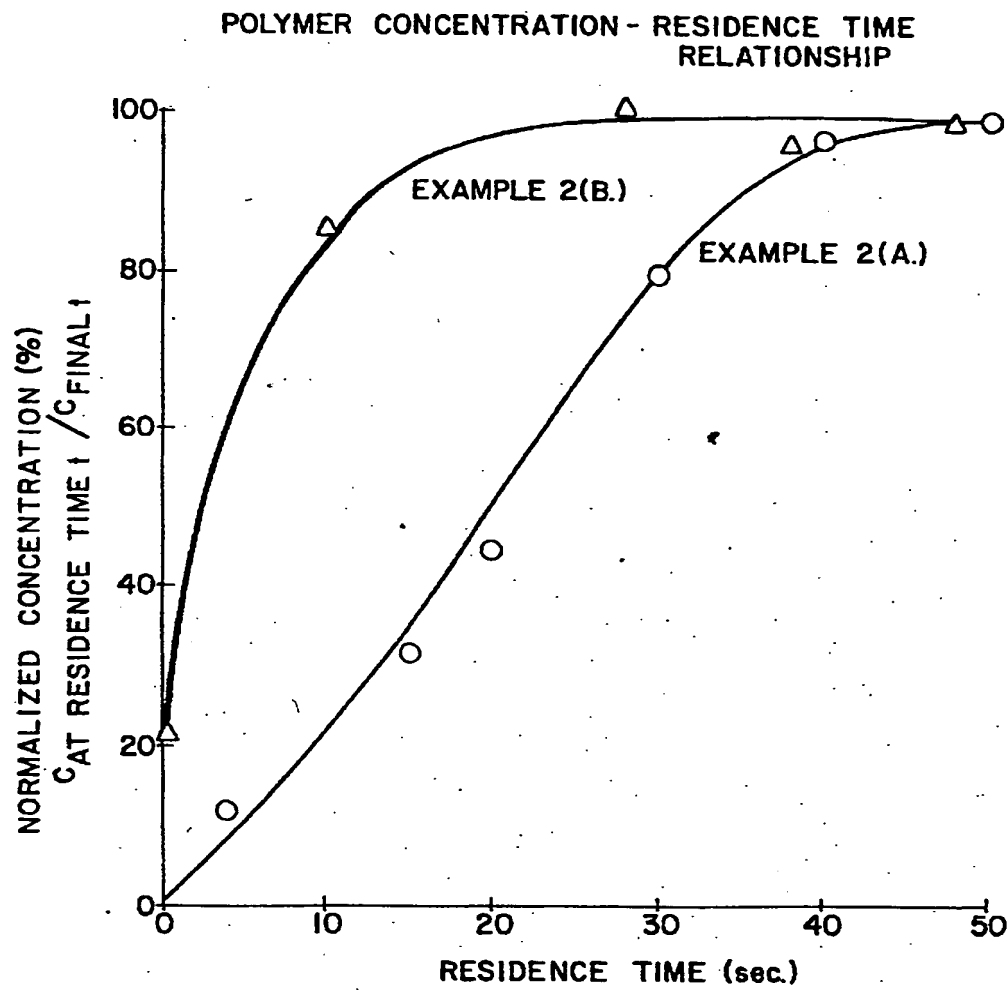


FIG. 5

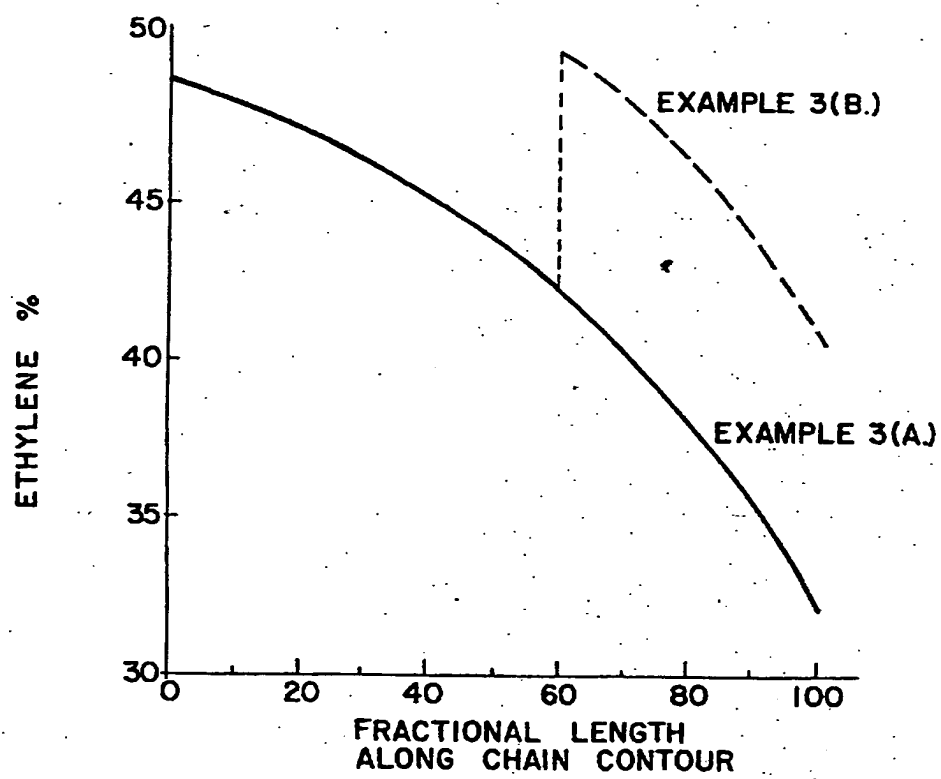


FIG. 6